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The effect of charge localization and structure on electron impact induced rearrangements of organic molecules

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THE EFFECT OF CHARGE LOCALIZATION AND STRUCTURE ON ELECTRON IMPACT INDUCED REARRANGEMENTS OF ORGANIC MOLECULES

by

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INTRODUCTION

The study of ion rearrangements is a remarkably fecund area for the present generation of mass spectroscopists. Such studies are imperative if the full benefits of element mapping and computerized structure elucidation are to be made available to organic chemists. Furthermore, studies directed toward a more complete understanding of the mechanisms of ion rearrangements and fragmentations are invaluable to those workers who are trying to understand the fundamental changes which occur in a molecule upon electron impact. Conversely, knowledge of the structure of the ion produced by electron impact is of great assistance in mechanistic problems.

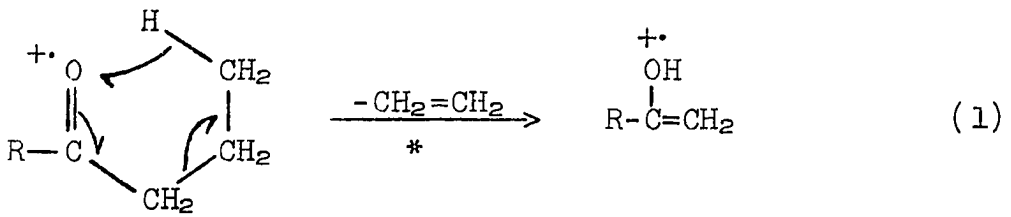
This work explores the question of charge localization effects upon ion structure and discusses bond formation occurring in unsaturated sulfoxides and sulfones. Ion rearrangement is defined as formation of bonds between atoms that were not bonded in the unionized molecule.

HISTORICAL

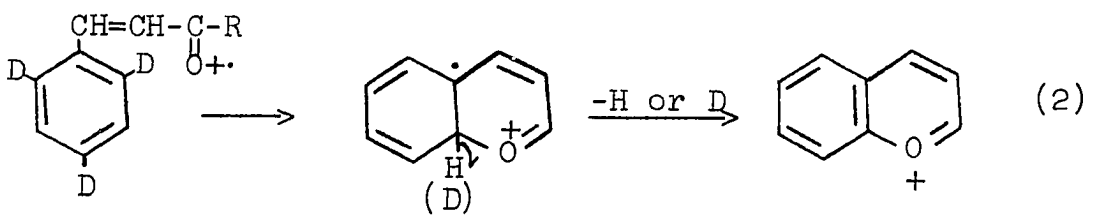
The Phenomenon of Mass Spectral Rearrangements

The present extensive use of mass spectrometry as an analytical tool for organic chemists could not have been foreseen only a few years ago. Suitable commercial instruments were available in the mid-1940's, but early studies of hydrocarbons revealed numerous rearrangement ions whose formation appeared to occur via random and unpredictable processes (1,2,3,4). These results discouraged those interested in the application of mass spectrometry to organic chemistry. But later workers found that the presence of groups with non-bonding or π-electrons in a molecule brought a measure of order to ion fragmentation (1). McLafferty has termed rearrangements controlled by functional groups "specific," as opposed to "random" rearrangements in alkanes and related compounds (5).

The hydrogen atom shows a strong proclivity for migration in electron-impact induced ions. Specific transfers, as in the "McLafferty" rearrangement, Eq. 1 (5), and scrambling, Eq. 2 (6), occur readily in many mass spectral ions. Hydrogen scrambling, even in aliphatic molecules, is a frequent occurrence and any mechanistic studies using deuterium as a label must be interpreted with care (7,8).



(1)

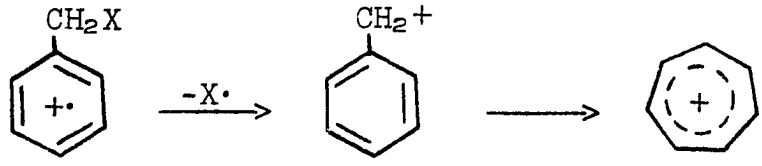


(2)

Bond formation between larger atoms occurs less frequently and is the subject of intense study, including several recent reviews (9,10,11,12).

The probability of a rearrangement occurring is related to the stability of the product ion, the stability of the product neutral fragment, and the ease of formation of the transition state of the reaction (1).

The ubiquitous tropylium ion (I), whose formation from numerous benzylic compounds has been proven by appearance potential (13) and labelling data (14,15,16) is probably an example of the stability of the product ion provoking



m/e 91

I

rearrangement. This stable ion is also often formed by more involved processes than that shown (see the Results and Discussion section of this work).

Wszolek, McLafferty, and Brewster (10) have examined a large number of bis-unsaturated compounds and concluded that the extent of rearrangement depends in large measure upon the stability of the expelled neutral fragment. Diphenyl ether, for example, undergoes rearrangement with expulsion of carbon monoxide to give an abundant ion at m/e 142, Eq. 3 (17). Diphenyl sulfide expels the less stable

$$\underset{\text{m/e 170}}{Ph_2O^{+\cdot}} \xrightarrow[*]{-CO} \underset{\text{m/e 142}}{(M\text{-}CO)^{+\cdot}} \qquad (3)$$

carbon monosulfide to a much smaller extent (17).

The effect of the transition state upon rearrangement, while undoubtedly important, is not easily determined. The "McLafferty" rearrangement has been shown to occur through a six-membered cyclic transition state, Eq. 1, but rearrangements occurring through three, four, five membered (1) and larger (18) transition states have been documented.

The formation of an ion containing atoms not bonded in the original molecule is, of course, prima facie evidence that rearrangement has occurred. More subtle rearrangements can be detected by appearance potential or labelling techniques, as in the previously mentioned tropylium ion.

Rearrangement ions can often be distinguished from ions that are the product of simple cleavage by reducing the energy of the ionizing electrons from the usual 70 ev to the 15-20 ev range. Rearrangements have a lower energy of activation than simple cleavages because bond formation as well as bond breakage is occurring (1,11). If this factor alone determined ion intensities, rearrangements would proceed at a faster rate and result in more intense ions than simple cleavages at any electron energy. However, another determinant in controlling the rate of fragmentation is the frequency factor, the pre-exponential term, ν, in equation 4. Equation 4 is derived from the

$$k = \nu \left(\frac{E-E_a}{E} \right)^{s-1} \qquad (4)$$

quasi-equilibrium theory of mass spectra (19) for the rate constant for ion decomposition where E is the internal energy of the ion, E_a is the activation energy, and s is the number of effective oscillators in the ion.

Frequency factors for rearrangement are low because of the ordering of the molecule required to attain the transition state (11,20). For simple bond cleavages frequency factors and activation energies are high relative to rearrangement and the energy imparted to a molecule by 70 ev electrons is more than enough for both cleavage and rearrangement. Rearrangement is therefore discriminated against because of the low frequency factor, although rearrangement peaks are often quite intense at 70 ev. Lowering the energy of the electron beam favors rearrangement over simple cleavage in two ways. The low energy electron beam may not impart enough energy to the molecule to provide the higher activation energy necessary for cleavage and the molecule, having less internal energy, will fragment at a slower rate. This will allow the rearrangement process, with its lower frequency factor, time to occur.

The fact that rearrangement is a slow process also means that the reaction may occur in part after the ion leaves the source. If decomposition occurs in a suitable field-free region a relatively abundant metastable ion may result (11,21). McLafferty and Fairweather (21) have shown that metastable abundances can be used to differentiate rearrangement processes from simple bond cleavage. They postulate that an abundant ion which does not exhibit an abundant metastable ion for its formation is not formed by a rearrangement process.

Charge Localization

Mass spectrometry became a viable analytical tool for organic chemists when it was discovered that non-bonding or π-electron sites controlled fragmentation and conventional mechanisms could be written for ion decomposition (vide supra). It seemed reasonable (and still does in many cases) to depict the ionized molecule as III, where X is any atom or group with non-bonding or π-electrons, rather than the more generalized II.

$$[R{-}X{-}R]^{+\cdot} \qquad\qquad R{-}\overset{+\cdot}{X}{-}R$$

II III

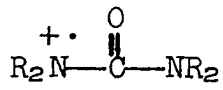
A large body of mass spectral literature has accumulated which assumes charge can be localized to an extent that rational fragmentation mechanisms can be written (3,22). A number of mass spectroscopists have attempted to learn whether one may truthfully speak of the charge or radical as being localized. The difficulty of such studies is that one can only observe the formation and decomposition of ions as they arrive at the collector. No product can be trapped or observed as in conventional chemistry and the lifetime of mass spectral ions is very short (10^{-5}-10^{-6} sec.).

Contradictory, and difficultly resolved, views have often been advanced, as in the postulation of both π (23) and n-electron (24) ionization in aromatic heterocycles such as pyridine.

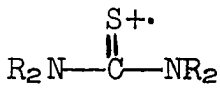
It should be noted that the concept of charge localization almost certainly does not involve initial electron removal from one site in the molecule. According to the quasi-equilibrium theory (19), an electron may be removed from any bond in the molecule to give an electronically excited species. This species may not decompose immediately and a rapid (relative to rate of decomposition) reorganization of electrons can place the charge at the site favored by resonance or low ionization potential (3).

Baldwin, et al. (25) in a study of ionization potentials (IP) of methylated ureas (IV) and thioureas (V)

concluded on the basis of comparisons with amines and thioketones that the charges could justifiably be considered as localized on nitrogen for the ureas and on sulfur for the thioureas. A similar conclusion was reached for semicarbazones and thiosemicarbazones (26).



IV



V

Junk and Svec (27) determined the ionization potential of a number of substituted alkanes and they believe that it is legitimate to consider the site of ionization to be isolated if one of the substituents has an ionization potential below that of the unsubstituted alkane.

A study of the elimination of neutral molecules such as water and acetic acid from steroids showed that the eliminations did not occur from either molecular or fragment ions when the charge was localized in another portion of the molecule by groups with low ionization potentials (28).

Localization of charge has also been named as a critical factor governing the decomposition of bibenzyl (29), trityl ethers (30), substituted 1-carbamoyl and 1-thiocarbamoyl-2-pyrazolines (31).

Occolowitz (32) showed that fragmentation could be controlled by the phenyl ring in a group of carbonyl

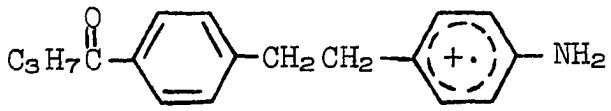
compounds, $Ph(CH_2)_nCOR$ ($n = 2,3$; $R = H$, OH, CH_3, OCH_3), when the energy of the ionizing electrons was just above the IP of the ring. At higher electron energies, the IP of the carbonyl group was reached and fragmentation patterns changed accordingly.

Shapiro and Tomer (33) found that substituents which lowered the IP of the ring in acetanilides and phenyl acetates (e.g., NH_2, OMe) appeared to localize more charge density on the ring.

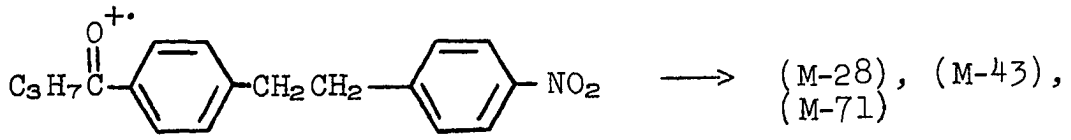
In spite of the above cited evidence Spiteller and co-workers (34) have questioned the need for charge localization on the basis of their work with aliphatic esters. Since they found that the McLafferty rearrangement occurred even though low IP substituents were present at another site in the molecule, they postulated that the rearrangement could occur without charge or radical localization at the carbonyl group. This opinion is not subscribed to by other workers (3, pp. 18-21 and 155-162).

Direct proof that the site of ionization can be controlled by substituents was obtained from the spectra of <u>para</u>-substituted butyrophenones, $YPhCOCH_2CH_2CH_3$ (35). Both McLafferty rearrangement and cleavage α to the carbonyl group were almost completely suppressed when Y = <u>p</u>-$NH_2PhCH_2CH_2$. Groups that did not suppress these fragmentations were H, $PhCH_2$, <u>p</u>-$NO_2PhCH_2CH_2$, and <u>p</u>-$C_3H_7COPhCH_2CH_2$.

The authors attributed the suppression of fragmentation to charge localization in the ring remote from the butyryl group (VI), as opposed to ionization on the carbonyl group or its attached ring (VII).



VI



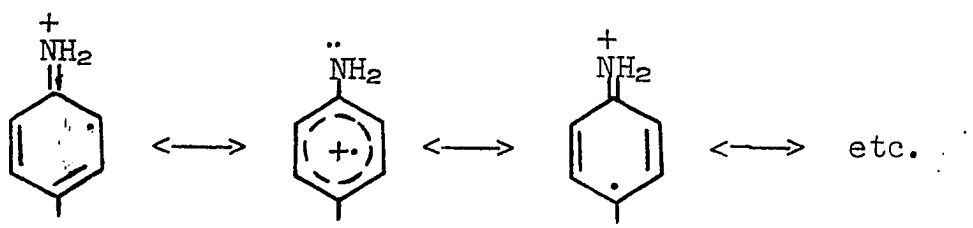
VII

The dramatic nature of this effect can be seen from the ion intensities in Table 1.

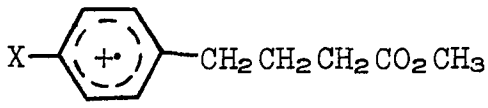
It is not clear whether charge localization in these compounds is caused by the lower ionization potential of the ring with the amino group attached, the resonance effect of nitrogen's lone pair electrons, or a combination of both.

Table 1. Characteristic ions in the 75 ev spectra of p-substituted butyrophenones (35)

Y	M	M-28	M-43	M-71	IP (ev)
H	100	28.9	470	230	9.38
$PhCH_2$	100	128	2650	47	8.69
p-$NO_2PhCH_2CH_2$	100	94	3000	2	9.10
p-$C_3H_7COPhCH_2CH_2$	100	99	2600	40	8.91
p-$NH_2PhCH_2CH_2$	100	<1	8	1	8.14

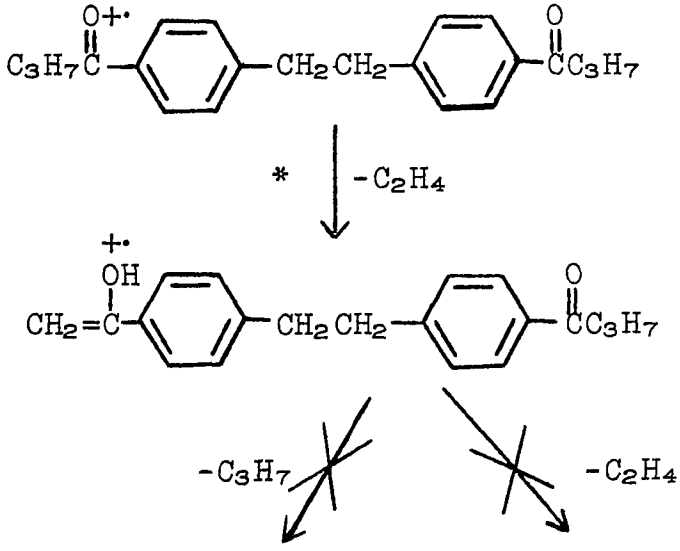


Charge localization on the benzene ring in methyl 4-phenylbutyrate also seems to be responsible for suppressing the McLafferty rearrangement and α-cleavage when X = Ph, MeO, and NH_2 (VIII) (36).



VIII

Charge transfer from one site in the molecule to another was considered unlikely by Wachs and McLafferty (35) since they found that such ions as ($M-C_2H_4-C_2H_4$) and ($M-C_2H_4-C_3H_7$) were of very low abundance in the p,p'-disubstituted bibenzyl system when the substituents were butyryl.



This viewpoint was strongly questioned by Mandelbaum and Biemann (37) as a result of their work with some substituted cyclopentanes. Both IX and X give double rearrangement ions and it was concluded that the charge

(and/or radical) site must have migrated through the σ-bonded insulating system. Numbers in parenthesis refer to ion intensities (Figure 1).

These workers conclude that the charge should not be considered as completely localized even if it has been shown to be present in a specific area of an ion at the time of its formation. They feel that the charge will be free to migrate to other areas in the ion, even if they are separated by several sigma bonds. In their opinion, this migration is governed by the ionization potentials of the various sites. It has been pointed out that charge should be able to migrate through an alkyl chain as long as the energy of the ionizing electrons is above the ionization potential of the chain (38).

In addition to the question of localization of charge, the location of the unpaired electron should be considered for odd electron ions. McLafferty (39) has proposed that a more satisfactory approach than charge localization involves separate consideration of the effect of the positive charge and radical sites. It is suggested that mechanisms which require homolytic bond cleavage are controlled by the radical and those involving heterolytic cleavage are controlled by the positive charge. An example is found in the two cleavages of aliphatic ethers shown below.

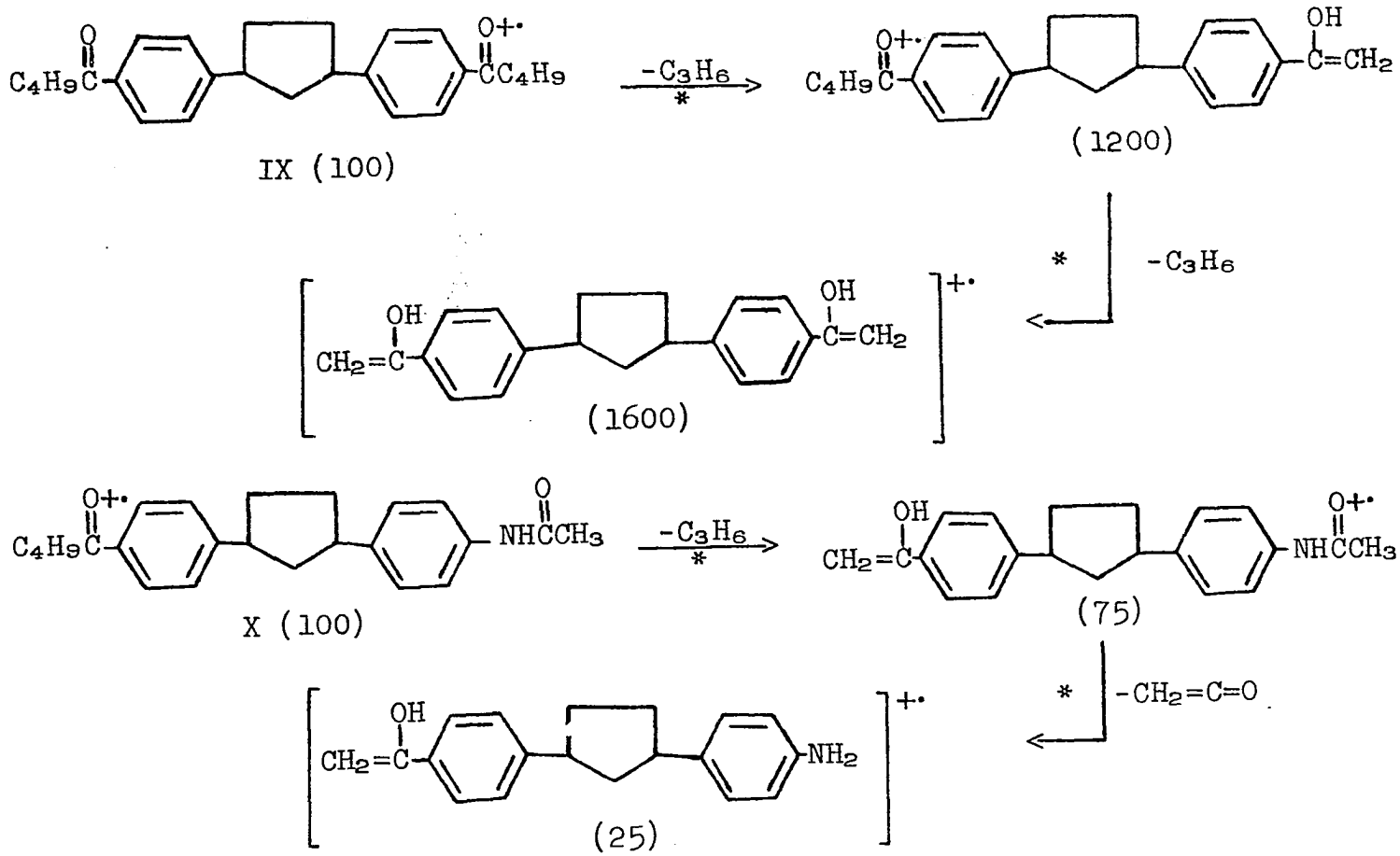
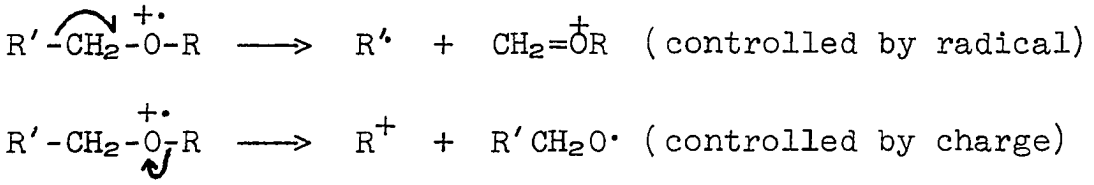


Figure 1. Charge transfer through σ-bonds in IX and X



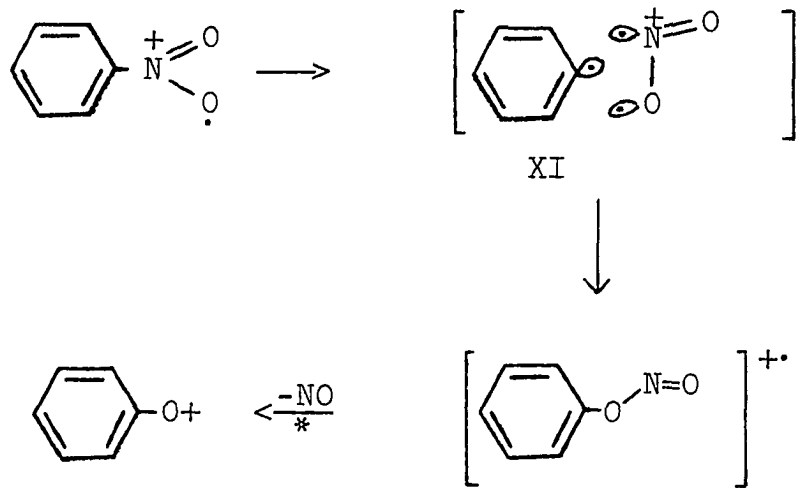
Separation of charge and radical site effects is not easy, although McLafferty's group has found evidence from substituent effects studies on butyrophenones (40) and triphenylcarbinols (41) that the unpaired electron in molecular ions furnishes an important driving force for rearrangement. However, Nicoletti and Lightner (42) found it difficult to arrive at a conclusion regarding radical and positive sites in their study of substituent effects upon the McLafferty rearrangement in n-butylbenzenes.

Objections have been raised by some who would prefer using the quasi-equilibrium theory (19) instead of charge localization for interpreting ion fragmentation (8,38). It is argued that localized charge structures are a naive and simplistic method for depicting ion structures, especially in view of the work of Mandelbaum and Biemann (37). In the quasi-equilibrium theory it is assumed that the energy of the excited molecular ion is rapidly and uniformly distributed over all accessible quantum states, subject to energy and angular momentum restrictions. It is further assumed that for a given internal energy there will be a marked tendency for low-lying electronic states

to be more highly populated (38). A substituent of low ionization potential is expected to introduce new, highly-degenerate low-lying electronic states. These in turn create a considerable fraction of ions which do not possess enough energy to undergo fragmentation at sites remote from the low IP substituent (8). Proponents of the quasi-equilibrium theory feel that localization of charge or radical character at the site of fragmentation is not necessary for fragmentation. They believe that enough vibrational energy in the appropriate vibrational degree of freedom is all that is required for fragmentation (8). Results to be discussed in the Results and Discussion section of this thesis seem to be in disagreement with these assertions.

The electron-impact induced fragmentations of nitro aromatic compounds have been extensively studied and reviewed (2,43). The most prominent mechanistic feature of their spectra is usually a large M-NO peak. This ion must arise via rearrangement to a nitrite ion and a mechanism has been written for the process (43).

Beynon and co-workers (43) noted that transition state XI is a three-center four-electron bond in the unionized molecule. The reaction becomes facile in the mass



XI

spectrometer because, in the words of the authors, "one of these electrons will be removed and a more favorable activated state is possible."

The rearrangement also occurs in photolytic processes (44) and a similar mechanism using electron excitation instead of electron removal can be written. However, it appears that electron removal or excitation may not be necessary for the process since thermolysis of nitrobenzene at 600°C gives some phenol, presumably from nitro-nitrite rearrangement (45), although these are rather brutal conditions.

Meyerson, Puskas, and Fields(46) discovered a substituent effect upon NO loss in substituted benzenes. Specifically, p-nitrobiphenyl, p-nitroaniline, and p-nitro-

phenol exhibit much greater loss of NO from the molecular ion than do the corresponding meta isomers.

A large energy loss accompanying ejection of NO was noted in the spectra of p-nitrophenol and p-nitrophenetole (47). This energy loss was attributed to the high activation energy required to effect the nitro-nitrite rearrangement.

Release of excess kinetic energy in a decomposition is detected by the observation of a "flat-topped" metastable ion for the process. Beynon, et al. (48), observed such a metastable ion for the M—NO process in ortho and para-aminonitrobenzene and derived an expression for the calculation of energy released.

$$d = \frac{4\, m_2^2}{m_1} \left(\frac{(m_1 - m_2)T}{m_2 eV} \right)^{\frac{1}{2}}$$

m_1 = parent ion
m_2 = daughter ion
d = width of f.t. m*(a.m.u.)
T = decrease in internal energy
e = electronic charge
V = accelerating voltage

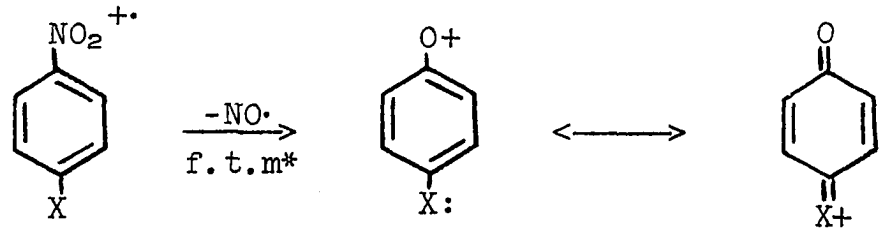
A thorough examination of 27 meta and para substituted nitrobenzenes by Bursey and McLafferty (49) revealed that, although a metastable ion appears for the M—NO process in each compound, the metastable ion is flat-topped for only five of the compounds studied. The substituents on these

five compounds are shown in Table 2, along with the calculated energy release (T).

Table 2. Energy released in $YC_6H_4NO_2^{+\cdot} \rightarrow YC_6H_4O^+$ (49)

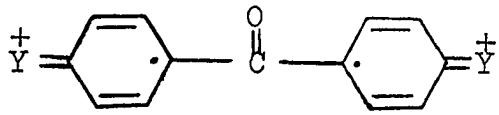
X	T (ev)
p-$N(CH_3)_2$	0.84 ± 0.02
p-NH_2	0.85 ± 0.04
p-OH	0.74 ± 0.06
p-OCH_3	0.56 ± 0.06
p-Ph	0.38 ± 0.06

Since the five substituents which gave a flat-topped metastable ion are electron donating by resonance, the authors proposed that energy was released due to product ion stabilization by resonance.

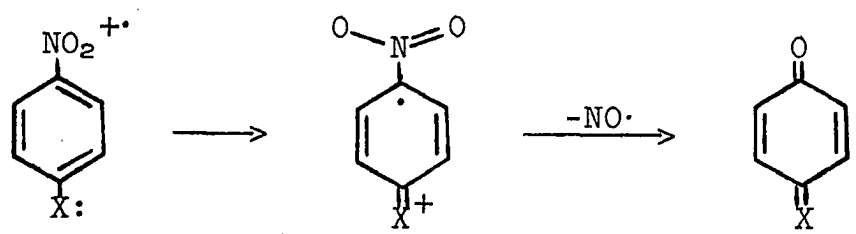


A study by the same authors (50) of substituent effects on the mass spectra of bibenzyls also gave dramatic support for the postulation that product ion stability is a major driving force for mass spectral reactions.

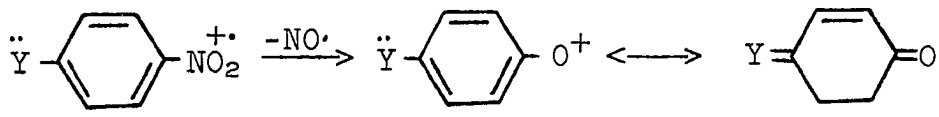
McLafferty and Bursey also studied the effect of substituents on the loss of CO from the doubly-charged molecular ion of benzophenones (51). They found that substituents which enhanced radical localization at the site of bond breakage (Y = NH_2, OMe, OH) caused the CO loss to increase.



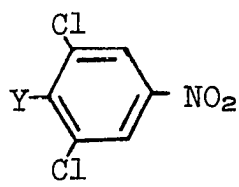
This suggested that partial localization of the radical site at the carbon atom attached to the NO_2 group might be an important driving force for the nitro-nitrite rearrangement, in addition to stabilization of the product ion of NO· loss (49).



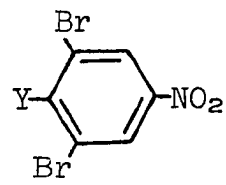
Bursey (52) provided elegant proof of the theory that resonance stabilization of the product ion could enhance a mass spectral process by demonstrating steric hindrance of resonance in XIII and XIV, Y = $(CH_3)_2N$ and Y = OMe.



XII



XIII



XIV

He measured the ratio of M-NO/M in these compounds with Y = OH as the standard. The dramatic decrease in the M-NO ion in those compounds where steric hindrance to resonance may occur is obvious from the ion intensities in Table 3.

Another feature of the spectra of nitroaromatics is loss of NO_2 from the molecular ion (2,43). Whether the origin of this ion is unrearranged nitrobenzene or a nitrite ion was

Table 3. Effect of steric hindrance of resonance on ion intensities (52)

Y	Z/Z_o[a] XII	XIII	XIV
HO	1.0	1.0	1.0
H_2N	1.2	1.0	0.70
CH_3O	1.4	0.06	0.08
$(CH_3)_2N$	0.83	0.04	0.03

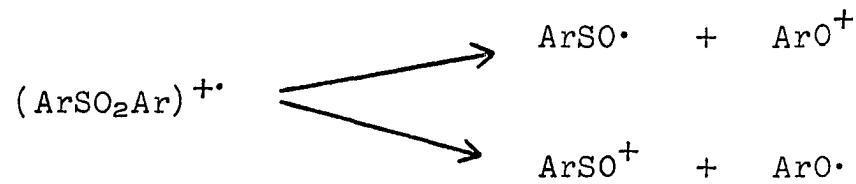
[a] $Z = (M-NO)/M$, Z_o ($Y = OH$).

considered recently by Shapiro and Serum (53). The ratio $(M—NO)/(M—NO_2)$ in some substituted nitrobenzenes was seen to increase as progressively lower energy electrons were employed. Since rearrangement ions (M-NO) normally increase relative to simple cleavage ions at low electron voltages (vide supra), it was concluded that the $M-NO_2$ process probably occurs from unrearranged nitrobenzene ions.

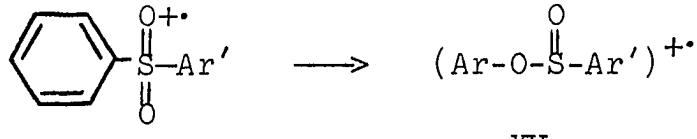
Rearrangements in Sulfoxides and Sulfones

Ions due to skeletal rearrangements are a prominent feature of the mass spectra of organosulfur compounds. Processes of the type A-B-C → A-C + B are very common, as are other isomerizations of the molecular ion. A large body of work has been devoted to these rearrangements and recent reviews are available (9,12).

The spectra of aryl sulfones contain prominent ions due to $ArSO^+$ and ArO^+ (54).



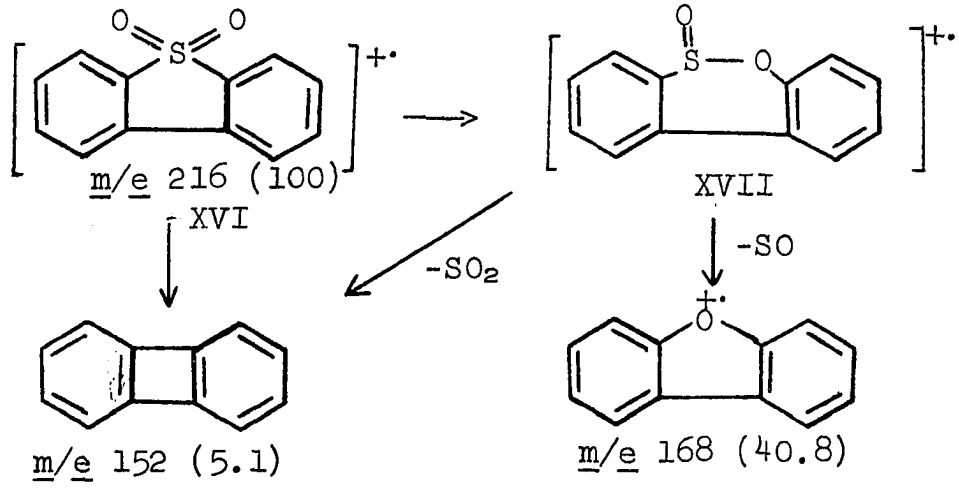
The authors feel that migration of an aryl group from sulfur to oxygen implies that the electron deficiency is largely localized in a nonbonding oxygen orbital. They suggest that interaction of the orbitals of the electron rich aryl group with the electron deficient center results in rearrangement to a sulfinate ion (XV), which can decompose to give the observed ions. It should be noted that charge localization on the ring could give the same result.



XV

Another rearrangement often observed is loss of a neutral fragment from the center of the molecule. It appears that SO loss from diaryl sulfoxides is stronger than SO_2 loss from the corresponding sulfones (55,56).

Surprisingly, SO loss is also stronger than SO_2 loss in XVI, even though SO loss probably occurs from a rearranged ion such as XVII (57).

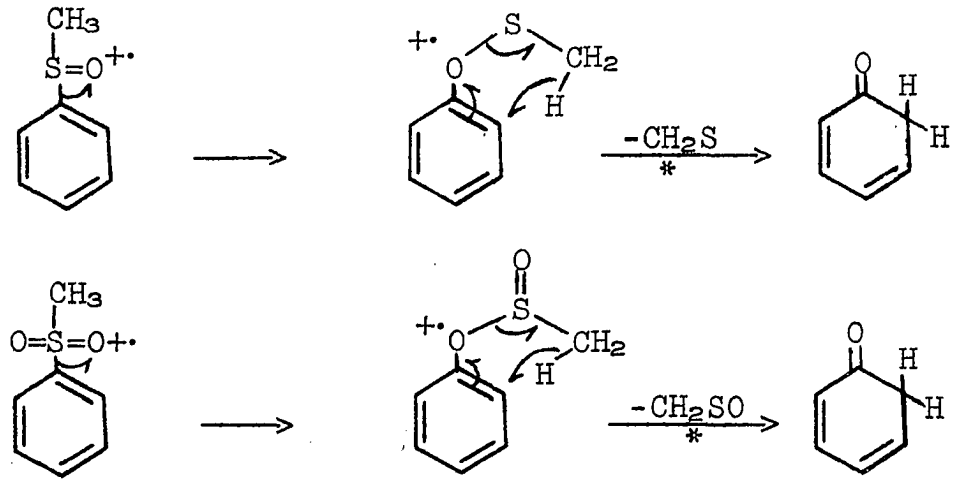


It is possible that both SO and SO_2 are lost from XVII and that SO loss predominates because dibenzofuran is more stable than biphenylene.

Compound XVI also undergoes successive losses of two molecules of carbon monoxide, indicating that both oxygen atoms become bonded to carbon in some manner.

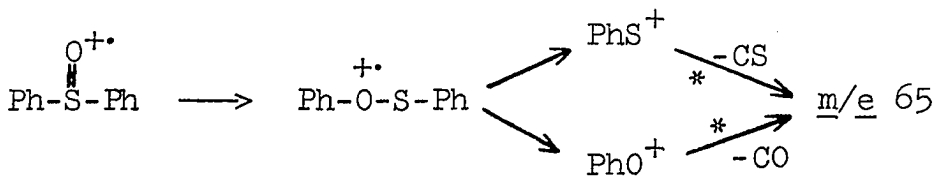
A rather extensive study of sulfoxides and sulfones (56) revealed that extensive C-O bond formation occurs in aromatic compounds, but no such rearrangement was noted for dialkyl compounds. Other work on alkyl sulfoxides (58) and sulfones (59) corroborated these results.

An interesting rearrangement leads to loss of CH_2S from methyl phenyl sulfoxide and CH_2SO from methyl phenyl sulfone. The following mechanisms are written for these processes (12,56).

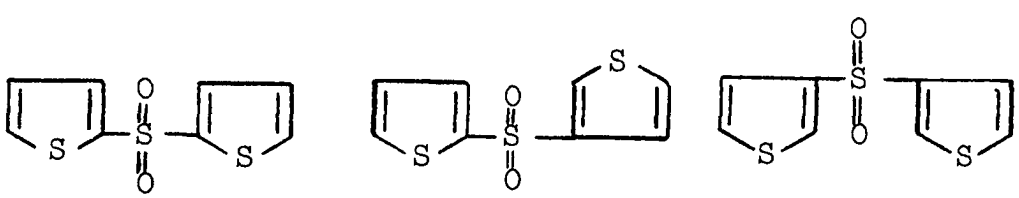


It seems likely that the expelled molecules are thioformaldehyde and thioformaldehyde S-oxide, the simplest sulfine. These molecules will be considered in detail in the Results and Discussion section.

Aryl sulfoxides were also shown to undergo a sulfoxide-sulfenate rearrangement in a manner analogous to that discussed for sulfones (56).

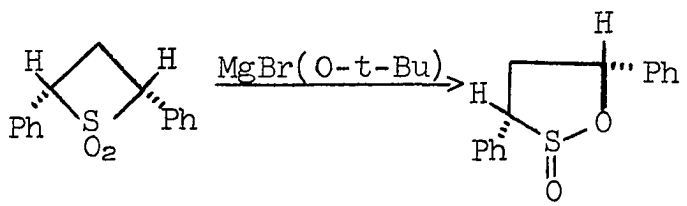


Migration of the thienyl group from sulfur to oxygen was observed in the spectra of the three dithienyl sulfones, XVIII-XX (56).

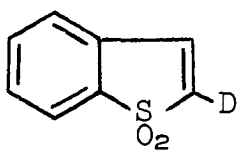


XVIII XIX XX

The formation of sulfenates from sulfoxides is responsible for thermal and photochemical stereomutation of sulfoxides (60) and sulfone-sulfinate isomerization has been shown to occur chemically (61).



Heiss, Zeller, and Zeeh (62) investigated C-O bond formation in cyclic sulfoxides and sulfones. The loss of CDO from the molecular ion of XXI indicates that C-O formation is specific, at least in this compound.

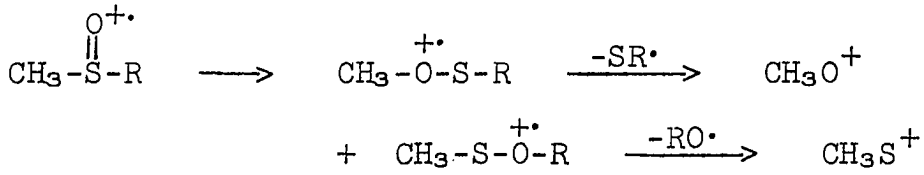


XXI

Other cyclic sulfones also undergo extensive C-O bond formation before decomposition (63,64).

The belief that aromaticity or unsaturation is required for sulfoxide-sulfenate and sulfone-sulfinate rearrangement (3,54) has been dealt a severe blow by recent high-resolution studies which prove the existence of CH_3S^+ and CH_3O^+ ions in the spectra of dimethyl sulfoxide (65) and methyl vinyl sulfoxide (66). No metastable ions are

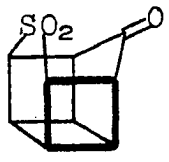
reported for their formation, but their existence is good evidence that methyl migration has occurred. Vinyl group



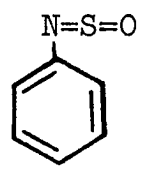
migration is also observed in the spectrum of methyl vinyl sulfoxide (66).

The loss of SO or SO_2 is a very common occurrence in unsaturated compounds. In addition to the diaryl sulfoxides and sulfones mentioned previously, such a loss occurs in methyl vinyl sulfoxide and sulfone (67). Loss of SO_2 is also observed in the mass spectra of sulfonyl ureas (68), sulfonylthioureas (69), and sulfonamides (70,71).

Caged keto sulfones (XXII) (72) and aryl sulfinylamines (XXIII) (73) lose SO_2 (XXII), SO (XXIII), and CO (XXII and XXIII) from the molecular ion.



XXII



XXIII

Many other bis-unsaturated compounds lose stable fragments from the center portion of the molecule. A recent review is available (10, and references contained therein).

The loss of CO from a rearranged form of the molecular ion is certainly not peculiar to sulfoxides and sulfones. Some other compounds in which this occurs are aromatic N-oxides (74,75), nitrones (76,77), aromatic azoxy compounds (78), azoxybenzenes (79), and β-nitro styrenes (3, chapter 16, 80).

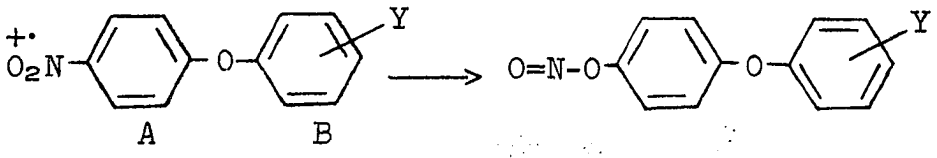
Carbon-13 labelling has demonstrated that the carbon atom lost in CO comes from the aromatic ring in some of these compounds (76,80).

RESULTS AND DISCUSSION

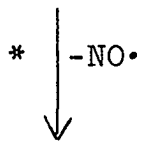
Charge Localization and Transfer

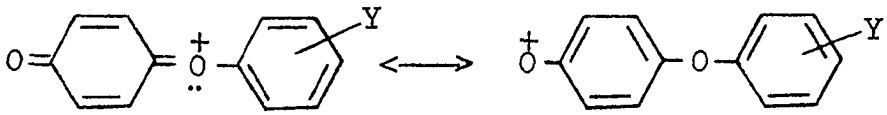
Charge localization

A priori, the loss of NO from the molecular ion of *p*-phenoxynitrobenzenes should be accompanied by a release of kinetic energy and the appearance of a flat-topped metastable ion. Bursey and McLafferty (49) showed that such an ion appeared in the spectra of nitrobenzenes with *para* substituents capable of stabilizing the product ion by resonance. A *p*-phenoxy group should also have this effect.



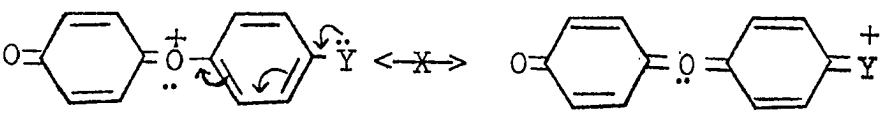
XXIV





This expectation is realized in the spectra of p-phenoxynitrobenzenes when Y (on ring B of XXIV) is an electron withdrawing atom or group. Substituents which are electron donating by resonance cause a radical change in the fragmentation pattern. Namely, the M-NO process is almost completely suppressed and the previously flat-topped intense metastable ion is no longer in evidence at all. The relative intensities of the M-NO and M-NO_2 ions in the compounds studied are given in Table 4. All spectra discussed in this thesis were taken at 70 ev unless otherwise specified.

This dramatic substituent effect cannot be attributed to product ion stabilization by resonance for three reasons that are independently self-sufficient. First, resonance forms which might be written for product ion stabilization by a substituent on ring B of XXIV must include a tetravalent ether oxygen with ten electrons in the valence shell (XXV) or an unlikely dipolar ion. Second, even if such a resonance form was tenable



XXV

Table 4. Effect of substituents on loss of NO and NO_2 from XXIV

Y	(M-NO)[a]	($M-NO_2$)	IP of PhY, ev (81)
H[b]	10.0	3.4	9.24
p-Br[c]	4.5	1.7	8.98
m-Br[c]	7.3	1.5	
p-Cl[b]	9.1	2.8	9.07
m-Cl[b]	12.9	2.4	
p-F[b]	7.5	2.9	9.20
m-F[b]	14.1	3.5	
p-CN[b]	20.8	4.4	9.71
m-CN[b]	21.4	4.2	
p-CF_3[b]	19.2	2.3	9.68
m-CF_3[b]	48.5	3.8	
p-NO_2[b]	20.0	4.0	9.92
p-CH_3	3.3	4.8	8.82
m-CH_3	6.2	2.5	
p-t-Bu	3.4	0.0	8.68
m-t-Bu	4.6	0.0	
p-OCH_3	0.0	3.3	8.22

[a]Molecular ion = 100.

[b]A flat-topped m* was observed for M → M-NO.

[c]A large, but not flat-topped, m* was observed for M → M-NO.

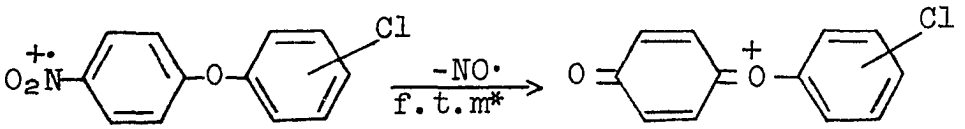
Table 4 (Continued)

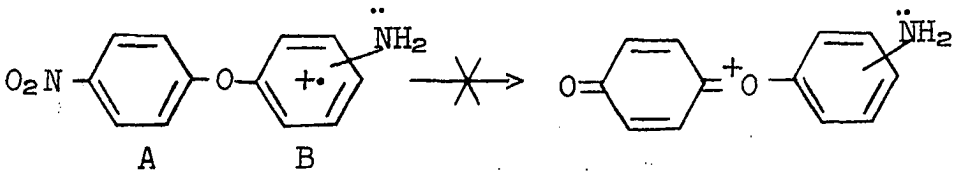
Y	(M-NO)[a]	($M-NO_2$)	IP of PhY, ev (81)
m-OCH_3	1.7	2.4	
p-Ph	1.1	3.2	8.27
m-Ph	0.0	2.0	
p-NH_2	0.4	19.1	8.70
m-NH_2	0.0	5.3	
p-OH	0.8	5.6	8.50
m-OH	2.2	2.2	
p-OPh	0.0	2.4	
m-OPh	0.0	0.0	

the substituent effect would be opposite to what is observed; that is, electron-donating groups would enhance the reaction instead of suppressing it. The third reason that product ion stabilization cannot be responsible for these results is that meta and para substituents have an essentially identical effect upon the M-NO process. Again assuming that resonance form XXV is possible, meta substituents in ring B should have no effect on product ion stability.

These results can be explained by invoking the concept of preferred localization of charge (27,35). A substituent

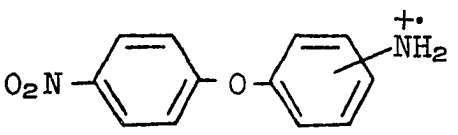
which can stabilize the charge on ring B prevents the nitro-nitrite rearrangement and subsequent loss of NO. The rearrangement is probably triggered by the unpaired electron in the non-bonding orbital of an NO_2 group oxygen atom (43). The failure of these substituents to affect the M-NO_2 process will be a subject for later consideration (<u>vide infra</u>).





XXVIa

The structure drawn for XXVIa is only a convenient method for depicting the charge on ring B. A canonical form, XXVIb, is just as valid.

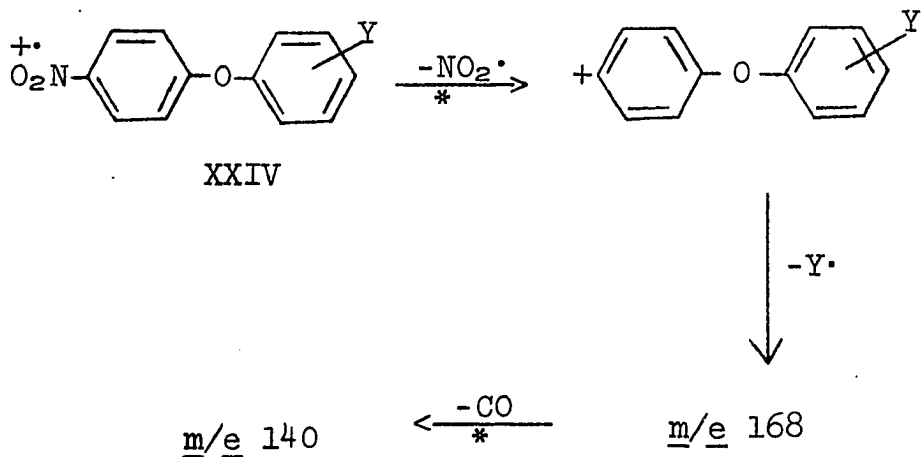


XXVIb

Localization of charge in ring B can cause fragmentation to occur at that locus. XXIV (Y = OCH_3), for example, loses the methyl group and XXIV (Y = OH) loses carbon monoxide, a common process for phenols (3, chapter 2). When Y is an amino group, however, one does not observe the loss of HCN from the molecular ion as might be expected (3, chapter 8).

When Y is an alkyl group (CH_3 or t-Bu) the charge is apparently distributed between the two rings, since both NO loss (without a f.t. m*) and loss of H· (Y = CH_3) or CH_3· (Y = t-Bu) can occur from the molecular ion.

Other fragmentations of the molecular ion are unremarkable. Simple cleavage on either side of the ether oxygen is common, as is loss of both substituents to give an ion at m/e 168 which decomposes by a loss of CO. The M-NO_2 ion also loses CO in some cases.



The question arises whether the localization of charge on ring B is due to resonance stabilization of the charge or the low ionization potential of the electron donating groups. The IP's of some substituted benzenes are included in Table 4 and it is seen that the substituents which lower the IP of the benzene ring also suppress the M-NO process in these ethers. Proponents of the quasi-equilibrium theory might therefore argue that the low IP substituents on ring B are creating new low-lying electronic states from which the M-NO process cannot occur.

Further consideration of these results leads to the conclusion that resonance stabilization of the charge in ring B is more likely to be responsible for suppression of the M-NO process than the low IP of these substituents.

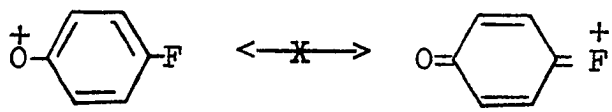
If the IP alone is the controlling element in determining where fragmentation can occur, no fragmentation of the nitro group should occur in these ethers. Since all of the substituents studied have a lower IP (on a benzene ring) than the nitro group, charge should be localized on ring B in all cases.

The meta and para chloro substituents, for instance, should cause the IP of ring B to be ca. 0.85 ev less than that of ring A (9.92 minus 9.07, Table 4), yet NO loss is strong and the flat-topped metastable ion indicates that energy is released in the process. Further lowering of the

IP of ring B by only 0.37 ev occurs when the chloro substituent is replaced by an amino group, but the M-NO process with its associated metastable ion is almost completely eliminated by this change.

It does not seem reasonable to expect such a dramatic transformation of the spectrum to occur upon such a modest lowering of the IP of ring B. It is proposed, instead, that the nonbonding and π electrons of groups which suppress the M-NO process create canonical forms (XXVIa and XXVIb) which localize the charge on ring B.

An apparent flaw in this proposal is the failure of the fluorine atom to stabilize charge on ring B. Carbonium ion stabilization by an α-fluorine atom does occur in the strong acid solutions studied by Olah and co-workers (82,83). Bursey and McLafferty included p-fluoronitrobenzene in their previously mentioned work on the M-NO process (49). The fluorine atom did not provide resonance stabilization of the phenoxy ion, in contrast to the electron donating substituents (Table 2).



It appears that no simple correlation exists between Olah's ions and electron impact induced ions. So the failure of fluorine atoms to localize the charge in ring B does not necessarily weaken the resonance stabilization of charge theory.

As noted previously, the M-NO_2 process is not affected by the character of the substituents on ring B, with the exception of the inexplicably large M-NO_2 ion when Y = p-NH_2.

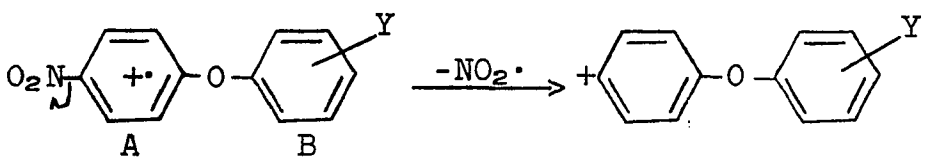
An increase in the (M-NO)/(M-NO_2) ratio in the low ev spectra of nitrobenzene has been interpreted to indicate that NO_2 loss occurs from an unrearranged ion, in contrast to the nitro-nitrite rearrangement required for NO loss (53). These ethers (XXIV) also showed an increase in the (M-NO)/-(M-NO_2) ratio at low ev.

The quasi-equilibrium theory can adequately explain simple bond cleavage (M → M-NO_2) with its supposition that sufficient vibrational energy in the appropriate vibrational degree of freedom is all that is required for fragmentation (8). However, rearrangement processes (M → M-NO) apparently require that the charge or radical be localized so that bond formation can occur.

The failure of the M-NO_2 process to respond to the substituents in ring B is in contrast to other systems in which charge localization suppresses both rearrangement and

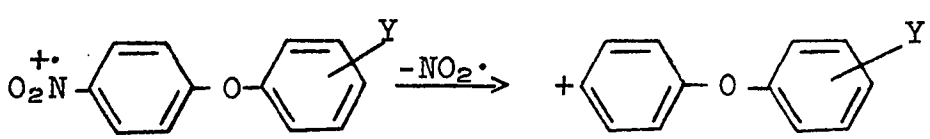
simple cleavage (35,36).

An intriguing, but very unlikely, possibility is that the M-NO and M-NO_2 processes are triggered by charge localization at different sites in the molecule. It has been postulated that the nitro-nitrite rearrangement is triggered by charge (and radical) localization on the nitro group (43). If the bond cleavage leading to NO_2 loss is triggered by charge localization on ring A (XXVII), then it is conceivable that this process might not succumb to the effects of resonance stabilizing groups on ring B, in contrast to the nitro-nitrite process.

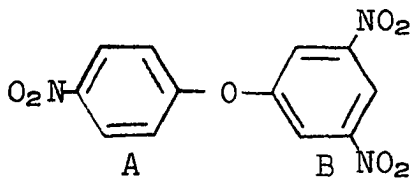


XXVII

It should be noted that charge localization on the nitro group requires heterolytic bond cleavage for NO_2 loss rather than the homolytic cleavage depicted for XXVII.



The theory of charge localization is further strengthened by the observation that NO loss does not occur in proportion to the number of nitro groups in the molecule. A statistical loss does seem to occur when Y = p-NO_2 vs. Y = H (XXIV, Table 4), but the spectrum (Table 5) of XXVIII shows only a small increase in the M-NO peak compared to XXIV (Y = p-NO_2).



XXVIII

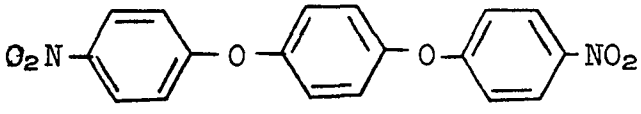
Table 5. Partial mass spectrum of XXVIII

m/e	Relative Intensity
305 (M^+)	100
275 (M-NO)	25
259 (M-NO_2)	3
229 (M-NO-NO_2)	7

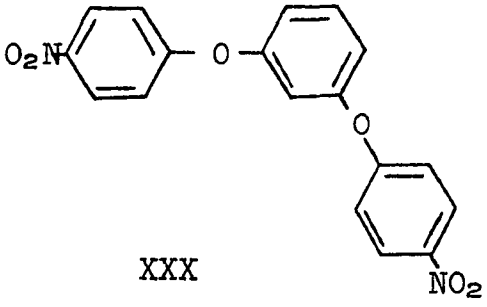
Even this increase may be partially discounted since the two nitro groups of ring B are in the meta position. It

can be seen in Table 4 that in all cases where NO is lost to a significant extent, groups in the meta position of ring B (XXIV) enhance the NO loss. It is possible that charge localized on the ether oxygen somehow affects the nitro-nitrite rearrangement. However, the ether oxygen must not control fragmentation since these compounds do not lose CO from the molecular ion, a common process in diphenyl ethers (17).

XXIX and XXX exhibited a flat-topped metastable ion for the M-NO process, although the M-30 peak was small (<2% of M^+).



XXIX

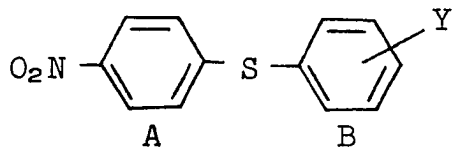


XXX

This indicates that electron donation by the phenoxy group (XXIV, Y = OPh) can be suppressed by the electron withdrawing nitro group. Of course, there still exists the possibility that this is due to a statistical effect of two nitro groups in the molecule (vide supra).

Measurement of the width of the flat-topped metastable ion for NO loss should give the amount of kinetic energy released in the process (48). The nitrobenzenes studied by Bursey and McLafferty (49) had energy losses of 0.38-0.84 ev, Table 2. Unfortunately, the instrument used in this study gave f.t. m* ions which were approximately the same width (3 amu) in all cases. So calculations of the differences in energy released in these molecules is meaningless, since the molecular weight of the molecules is the only variable. The calculated energy release varies from 0.77 ev (Y = CF_3) to 1.15 ev (Y = H). The proximity of these values to those of Bursey and McLafferty (49) is an indication that resonance stabilization of the product ion by the phenoxy group is energetically similar to stabilization by the substituents studied by these workers.

Five thioethers were examined to determine if the charge localization effects were similar to those found in ethers. Also of interest was the possible transmission of electronic effects through the sulfur atom. Table 6 gives the pertinent ion intensities for these sulfides (XXXI).



XXXI

Table 6. Effect of substituents on loss of NO and NO_2 from XXXI

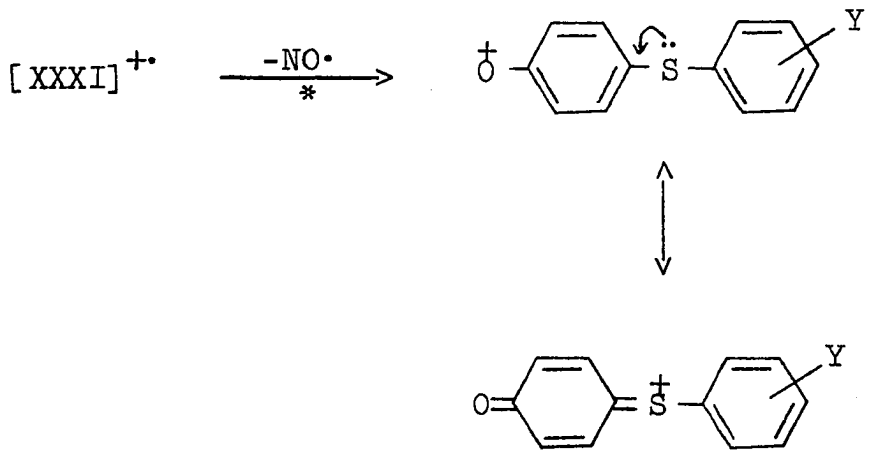
Y	M	M-NO	M-NO_2
H[a]	100	5.2	13.4
p-Cl[b]	100	6.7	6.7
p-Br[b]	100	7.7	4.6
p-NH_2[c]	100	3.3	16.7
m-NH_2	100	0.0	11.0

[a]A f.t. m* was observed for M → M-NO.

[b]A large, but not f.t. m* was observed for M → M-NO.

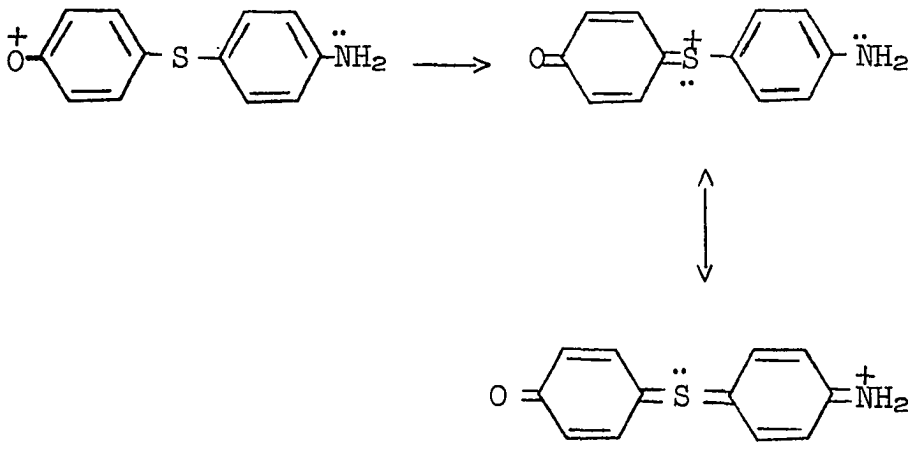
[c]A small m* was observed for M → M-NO.

The loss of NO from the molecular ion is a favorable process in these compounds, as in the ethers, when Y is an electron withdrawing group. Therefore, the thiophenoxy group can be added to those which stabilize the M-NO ion.

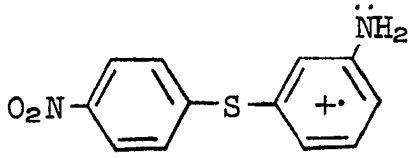


The p-NH_2 group does not suppress the M-NO process as completely as it does for the ethers studied. In fact, the weak m* observed for the M-NO ion in XXXI (Y = p-NH_2) is the first m* to be seen for ethers or thioethers with an electron donating group on ring B.

It is possible that the p-NH_2 group is providing further resonance stabilization for the product ion of NO loss by transmission of electronic effects through tetravalent sulfur. This resonance form is possible for sulfur because of the presence of low-lying unfilled d orbitals (84, p. 43). Transmission of electronic effects through sulfur in diphenyl sulfides also occurs in solution (85, and references contained therein).



Further proof that this type of stabilization is occurring is found in the spectrum of XXXI (Y = m-NH_2). The meta amino group cannot contribute to resonance stabilization of the M-NO ion, so charge localization effects should predominate. As expected, NO loss does not occur from the molecular ion of this compound.



The preceding discussion illustrates the difficulty of interpreting charge localization effects. Both the meta and para amino substituents should stabilize the charge on ring B of XXXI, yet some charge leaks to ring A and allows

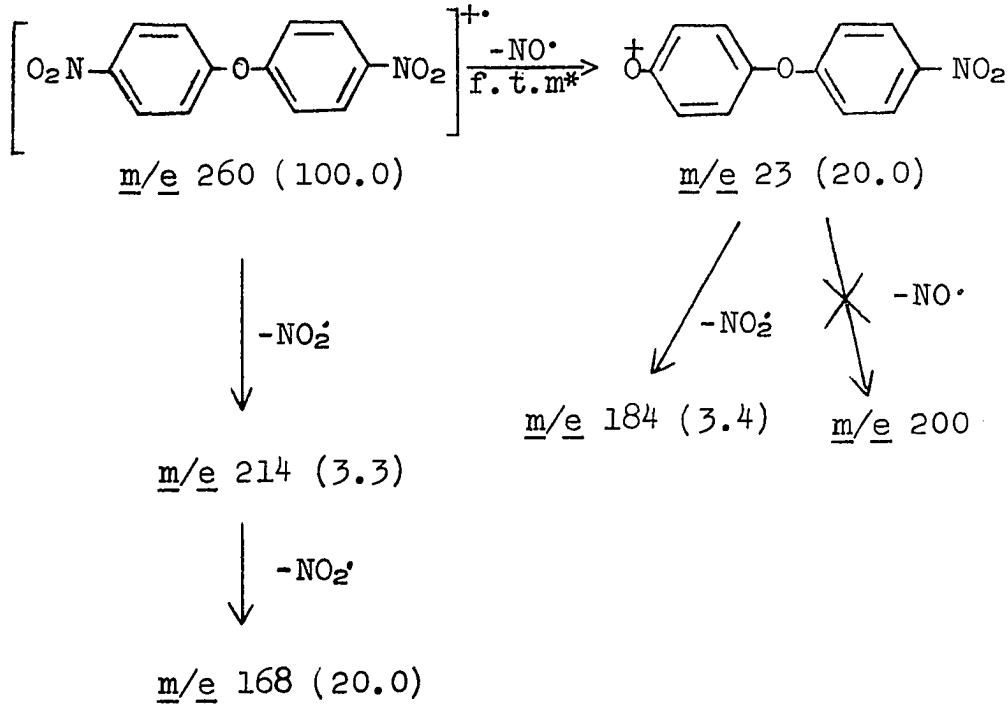
the nitro-nitrite rearrangement to occur when Y = p-NH_2. But if the charge is truly localized on ring B when Y = m-NH_2, why is it not so localized when Y = p-NH_2? It appears that an answer to this and other questions must await more detailed knowledge about ion fragmentation theory.

Charge transfer

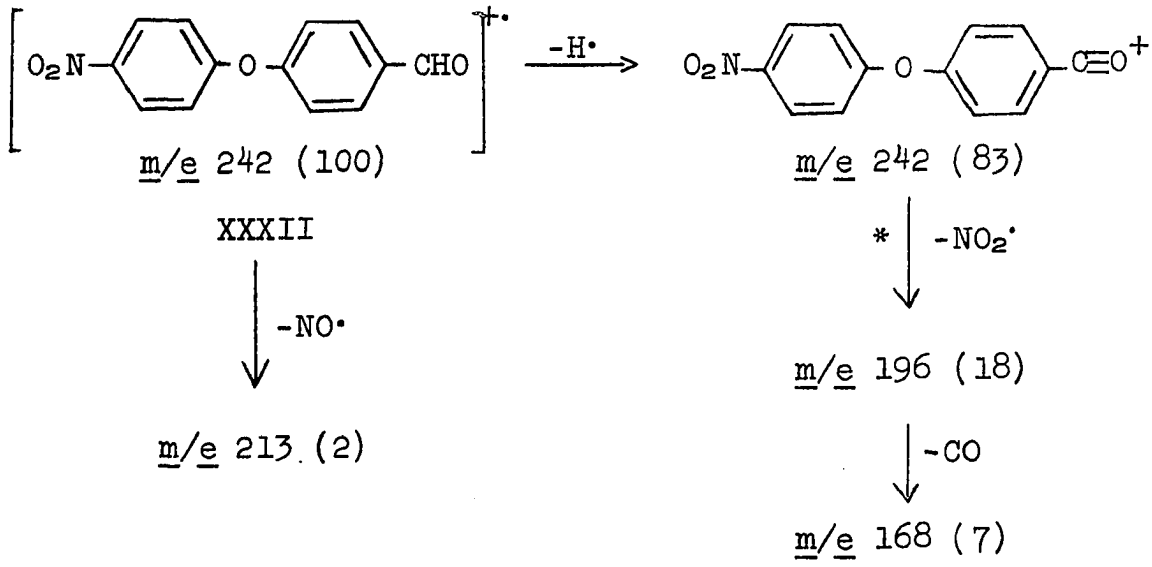
While the site of charge localization in the molecular ion can often be predicted and even controlled, the transfer of charge in fragment ions occurs in less predictable fashion. This discussion will refer only to charge transfer which leads to rearrangement of ions since it has already been shown that simple bond cleavages are not responsive to charge localization effects.

The ethers (XXIV) in which fragmentation occurred in ring B (Y = OCH_3, t-Bu) did not undergo NO loss from the M-15 ions. Furthermore, successive losses of NO were not observed in the spectrum of XXIV (Y = p-NO_2), although NO_2 was lost from both the M-NO and M-NO_2 ions.

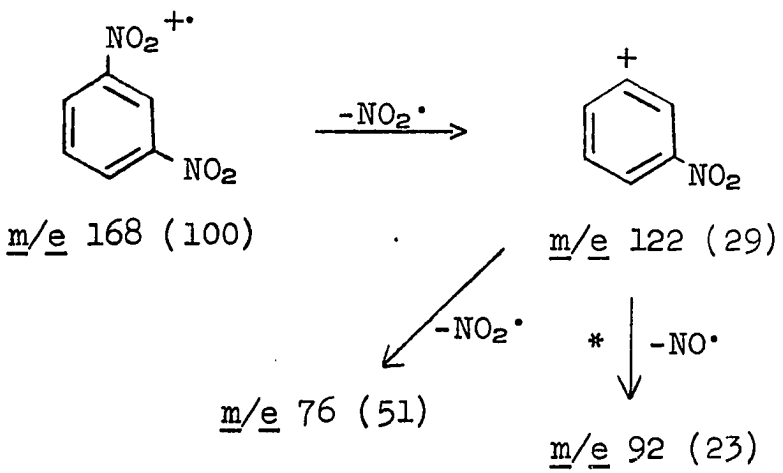
The M-1 ion in XXXII followed the same pattern; an abundant loss of NO_2 but no nitro-nitrite rearrangement and



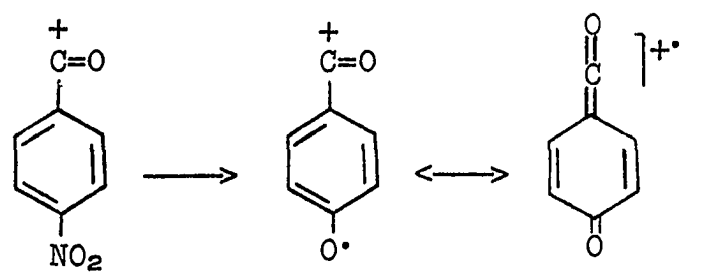
subsequent NO loss. An interesting feature of the spectrum is that NO_2 rather than CO is lost from the M-1 ion.

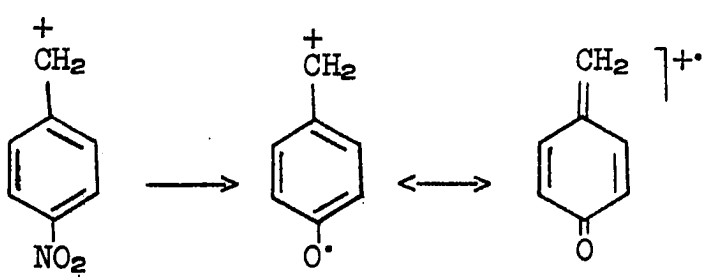


The failure of these ions to lose NO is probably not due simply to their even-electron character. Loss of NO from the even-electron M-NO_2 ion is observed in the spectrum of m-dinitrobenzene. Shapiro and Serum (53) have also



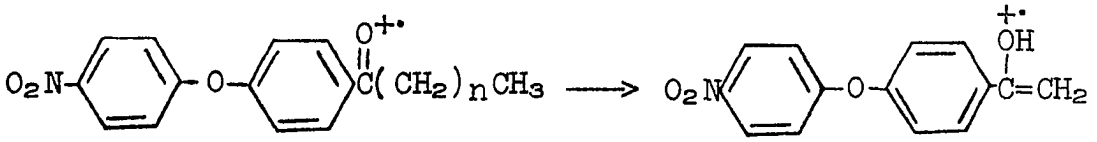
observed NO loss in some even-electron ions.





The failure of charge to migrate in fragments derived from XXIV is initially surprising, in view of the observation of successive rearrangement processes by Mandelbaum and Biemann (37). However, the charge transfer observed by these workers occurred in odd-electron ions. They feel that charge transfer should be a less favorable process in even-electron ions since decoupling of electrons to form a diradical ion is required (37).

In order to determine whether charge transfer leading to rearrangement could occur in odd-electron ions of diphenyl ethers 4-(4-nitrophenoxy)butyrophenone (XXXIIIa, n = 2) and 4-(4-nitrophenoxy)valerophenone (XXXIIIb, n = 3) were prepared. Partial spectra of these two compounds are given in Table 7.



XXXIII XXXIV

The odd-electron ion (XXXIV) that is the product of McLafferty rearrangement (m/e 257) also fails to undergo the nitro-nitrite rearrangement, demonstrating that even and odd-electron ions behave similarly in these diphenyl ethers.

Table 7. Partial mass spectra of XXXIII (a and b)

m/e	Relative Intensity XXXIIIa	XXXIIIb
299		11.8
285	17.6	
257	14.7	100.0
242	100.0	96.0
196	23.6	24.1
168	5.9	5.9

A possible reason for the failure of charge to migrate to the aromatic ring containing the nitro group is the strong electron-withdrawing character of this group. It may be that the positive charge simply will not migrate to the ring which is already electron deficient.

Compounds in which successive McLafferty rearrangements might occur were examined since the results of Wachs and McLafferty (35) and Mandelbaum and Biemann (37) were obtained with such compounds. Wachs and McLafferty (35) observed no charge transfer when ethylene was lost from a butyryl group as a result of McLafferty rearrangement. Mandelbaum and Biemann (37), on the other hand, observed successive losses of propylene from the valeryl groups in

their work. A more complete discussion of these two references can be found in the Historical section of this thesis. The loss of propylene is a much more favorable process than the loss of ethylene (86), so there was a possibility that this was responsible for the observation of charge transfer by Mandelbaum and Biemann.

4,4'-Oxydibutyrophenone (XXXV) underwent a McLafferty rearrangement to give an ion at M-28. No further loss of ethylene occurred from this ion, in agreement with the results of Wachs and McLafferty (35). To determine whether the oxygen atom was inhibiting charge transfer, the corresponding biphenyl (XXXVI) was examined. Again, successive McLafferty rearrangement ions were not observed. The fragmentation patterns for these compounds are given in Figures 2 and 3. It should be emphasized that McLafferty rearrangement occurs only from the molecular ion of these two compounds. No loss of 28 mass units from fragment ions is observed.

Since charge transfer occurred when loss of propylene from valeryl groups was involved (37), the divaleryl ether (XXXVII) and biphenyl (XXXVIII) were prepared. These compounds did undergo successive losses of propylene, as evidenced by metastable ions for the transitions. Figures 4 and 5 contain the fragmentation patterns of these two compounds.

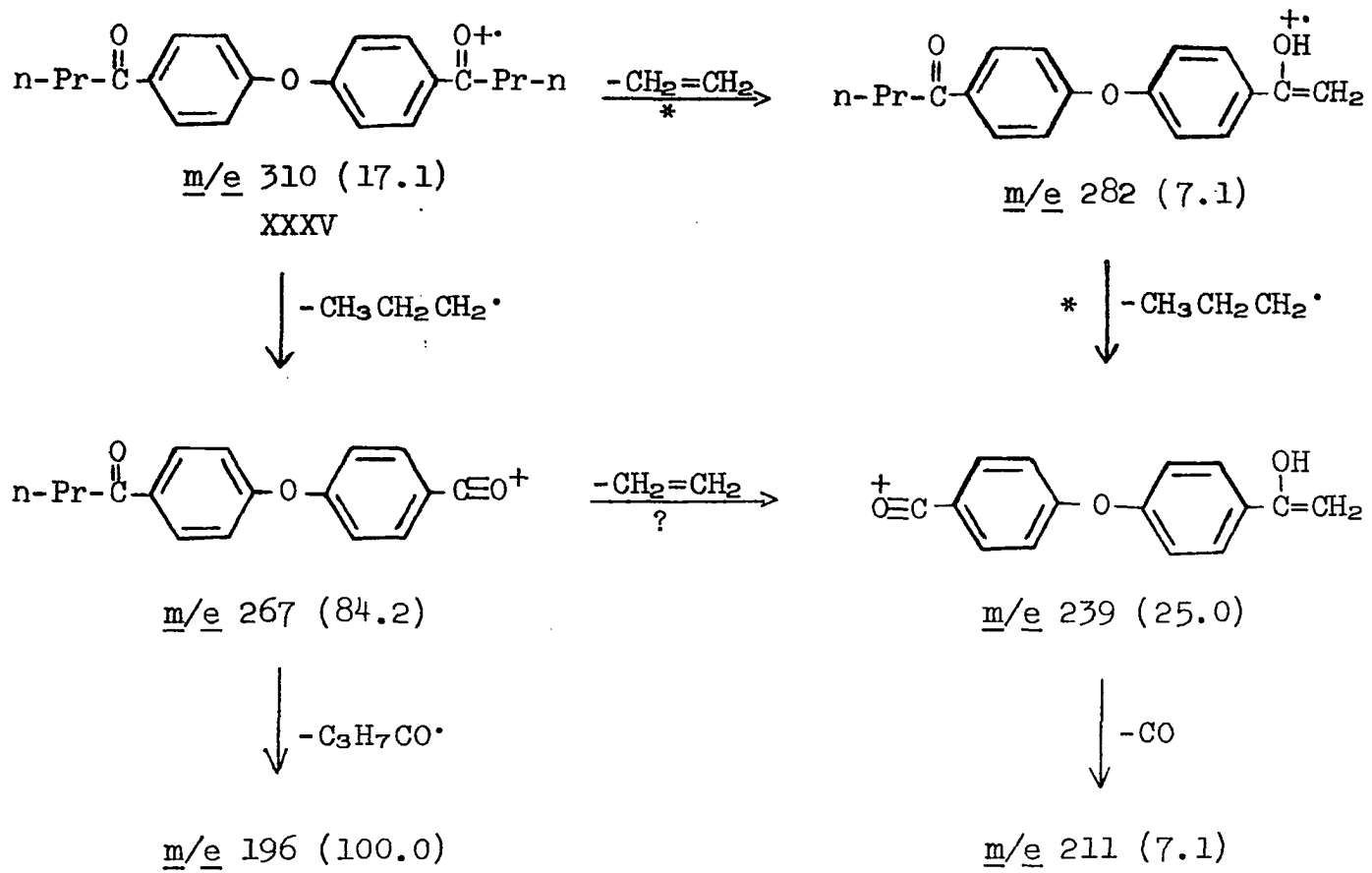


Figure 2. Fragmentation scheme for XXXV

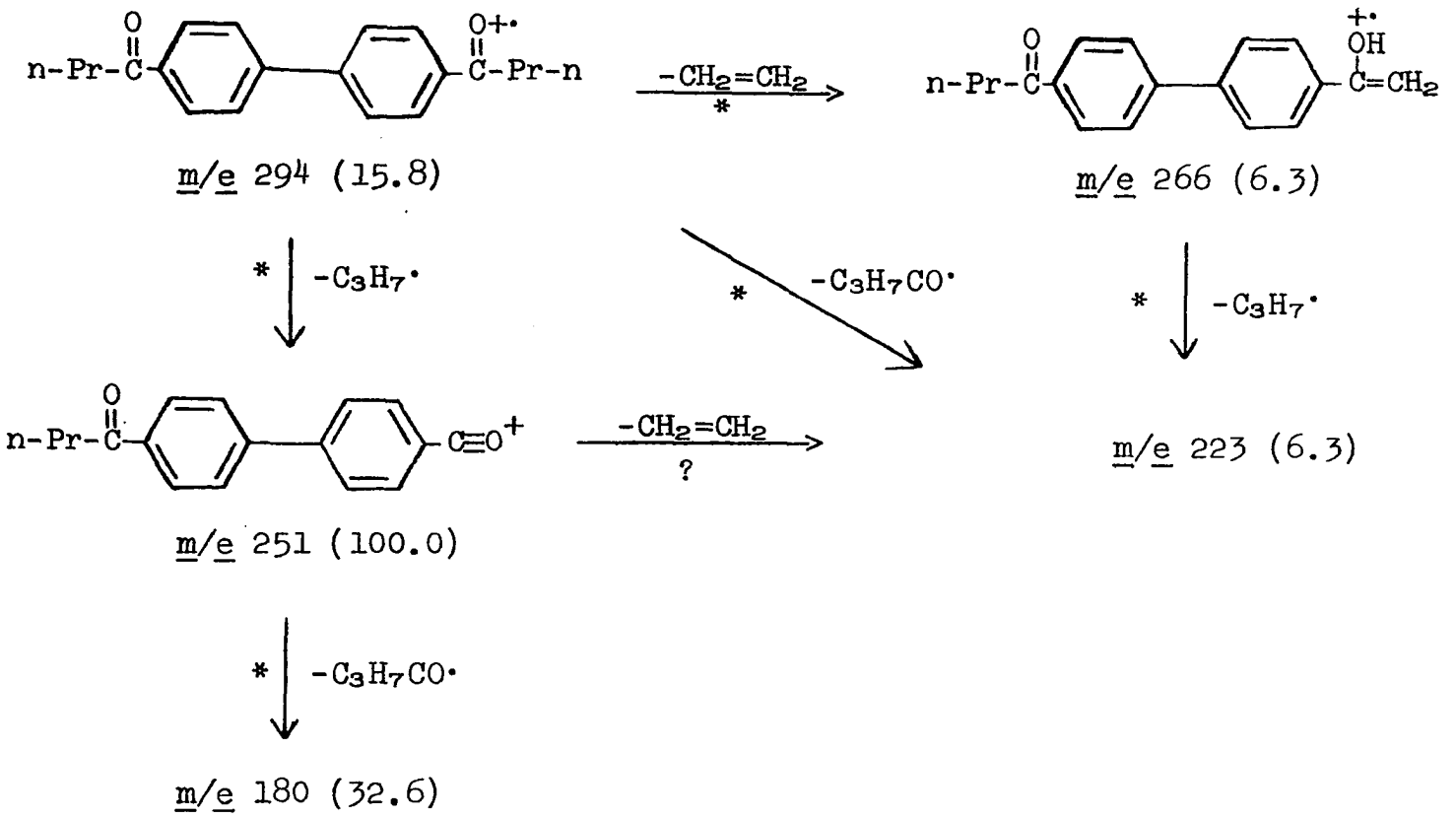


Figure 3. Fragmentation scheme for XXXVI

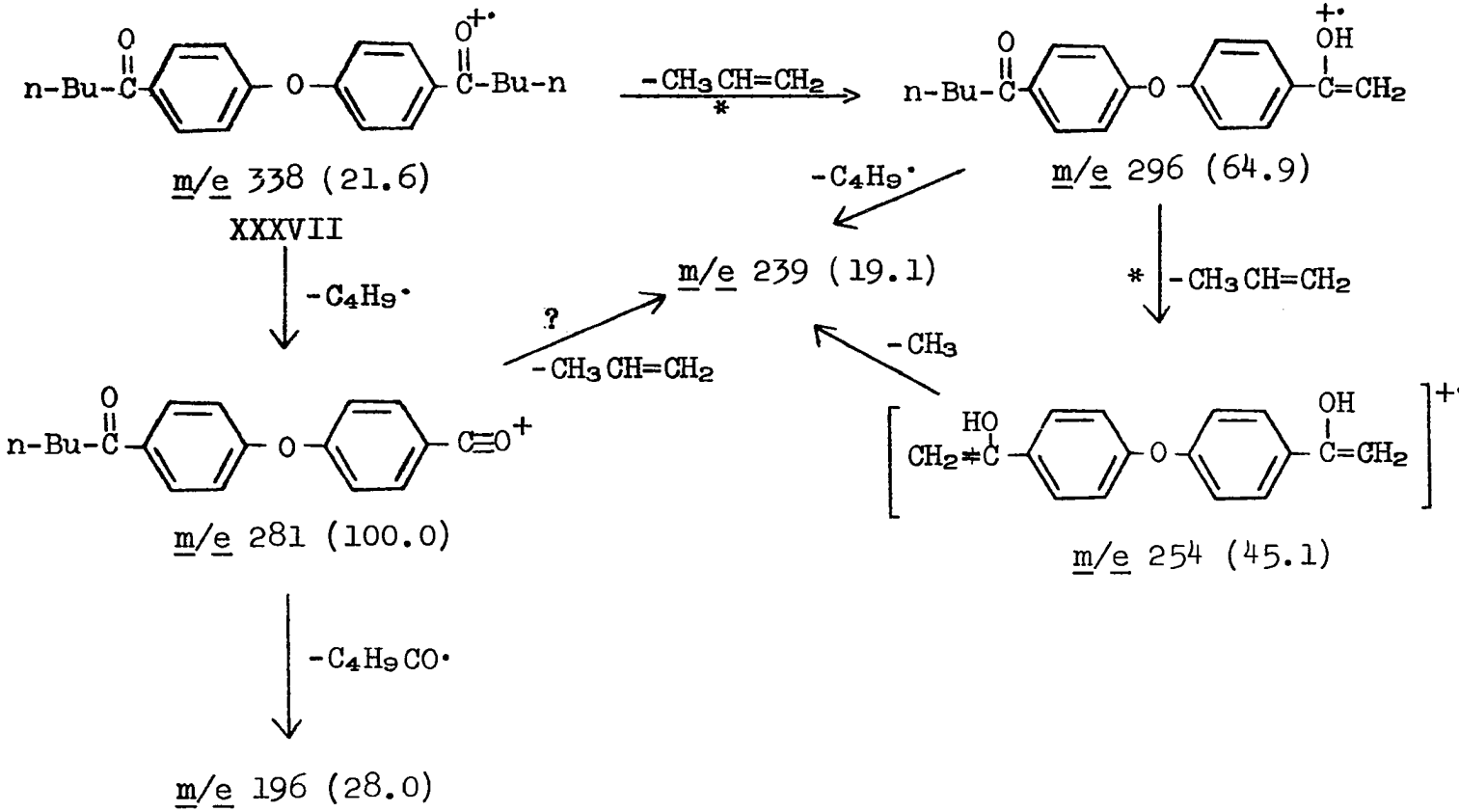


Figure 4. Fragmentation scheme for XXXVII

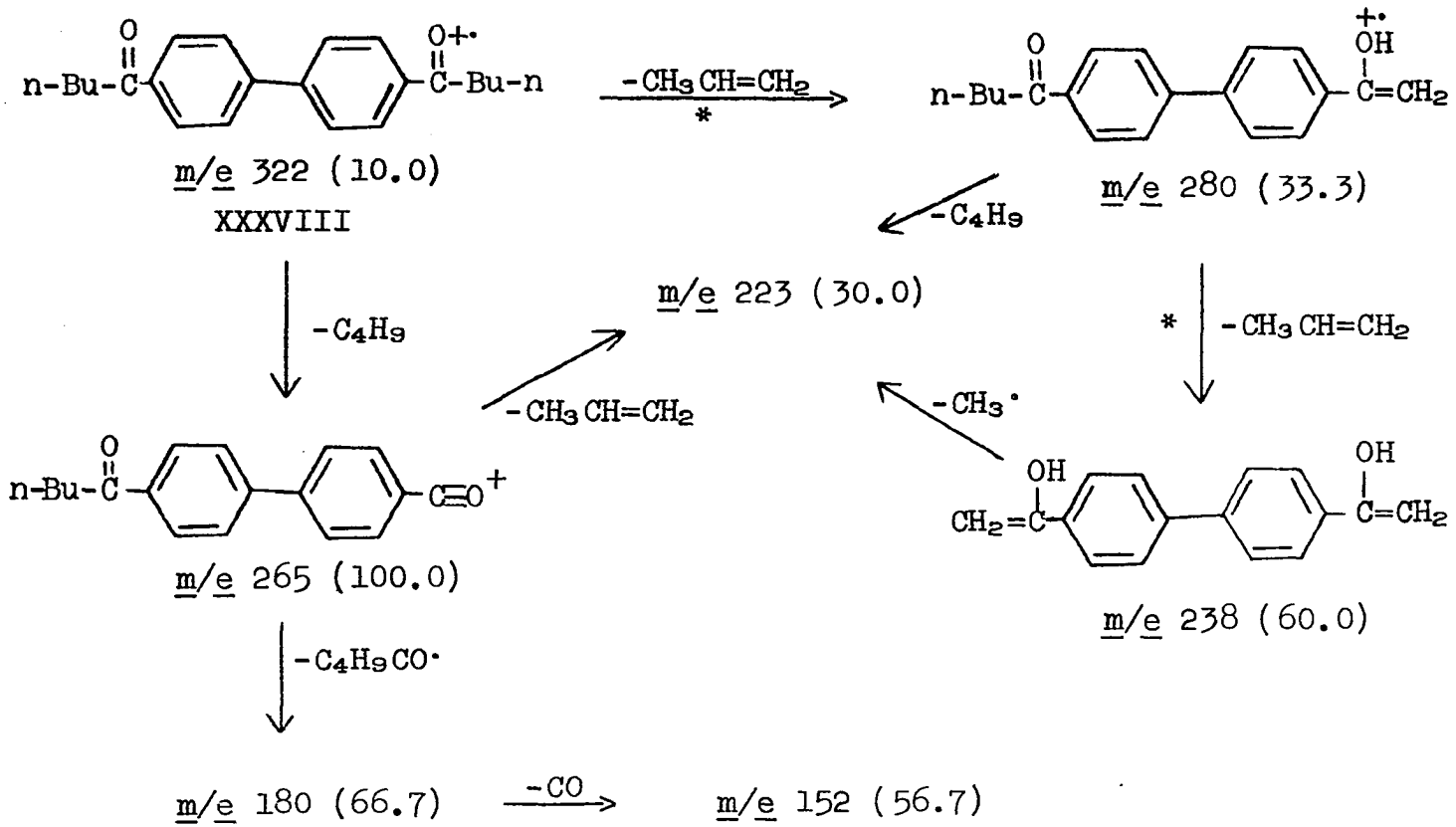
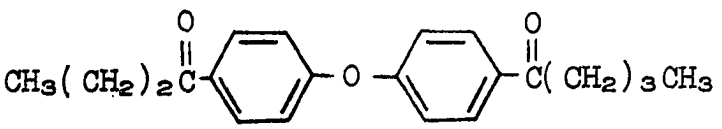


Figure 5. Fragmentation scheme for XXXVIII

Formation of the m/e 239 ion in XXXV and XXXVII and the m/e 223 ion in XXXVI and XXXVIII could indicate that McLafferty rearrangement (with charge transfer) is occurring in even-electron ions. Unfortunately, no metastable ion confirms the process and other equally plausible pathways exist for formation of these ions.

It is not at all clear why charge transfer occurs in ions derived from propylene loss but not from ions derived from ethylene loss. Loss of propylene is a very favorable process compared to loss of ethylene, presumably because a secondary rather than primary hydrogen is being transferred to the carbonyl group (86). The very low activation energy for propylene loss may allow it to occur twice. Another possibility is that the ion remaining after the initial propylene loss contains sufficient energy to cause charge transfer, while the M-C_2H_4 ion cannot effect transfer of charge.

In the hope of differentiating between these two possibilities, XXXIX was prepared. The presence of the



XXXIX

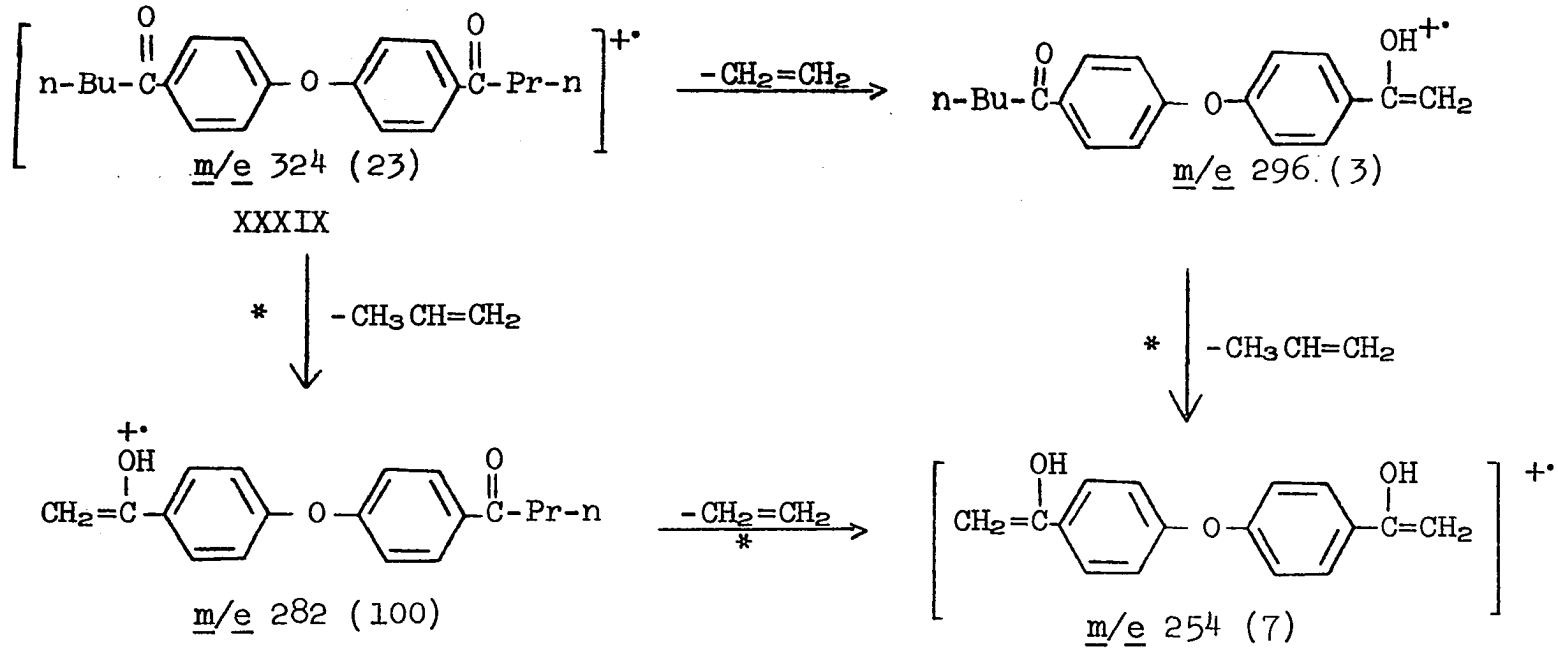
valeryl and butyryl groups in the same molecule should cause both ethylene and propylene loss to occur from the molecular ion. If the M-C_2H_4 ion loses propylene, the first statement would be substantiated. But if ethylene is lost from the M-C_3H_6 ion, the second statement would seem more truthful.

Amazingly, both of these processes occur. Metastable ions confirm the loss of 28 mass units from the M-42 ion and the loss of 42 mass units from the M-28 ion. The fragmentation pattern is given in Figure 6.

It is clear that prediction of charge transfer in fragment ions is a rather inexact science. While much effort has been expended on the theory of mass spectra, only the very tip of the iceberg has been uncovered.

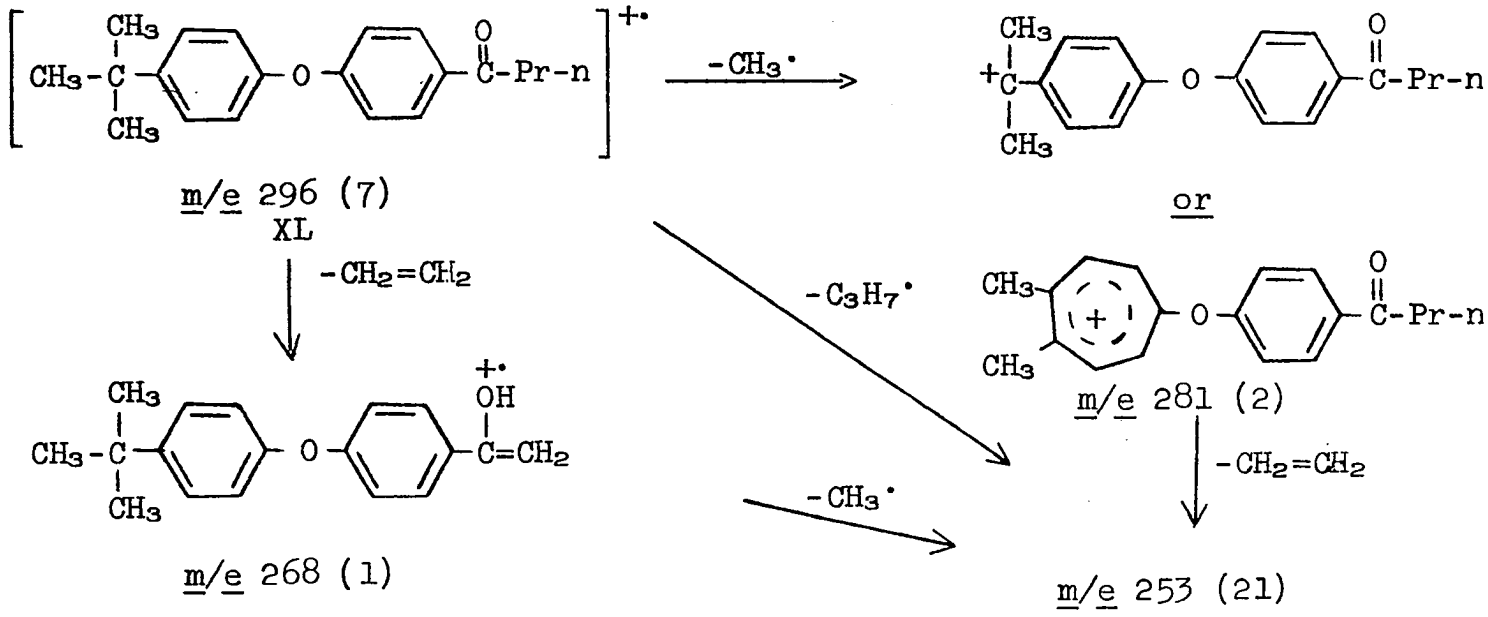
One other compound was studied in an effort to detect McLafferty rearrangement in an even-electron ion. The process has been observed in such ions previously (87,88,89), but charge transfer over several bonds was not involved.

4-(4-t-Butylphenoxy)butyrophenone (XL) yields an even-electron ion at m/e 281 by loss of a methyl group from the molecular ion. The ion at m/e 253 may result from McLafferty rearrangement and loss of ethylene from m/e 281. However, two other possible modes of formation of the m/e 253 ion exist; loss of $CH_3\cdot$ from m/e 268 and loss of $C_3H_7\cdot$ from the molecular ion, Figure 7. Regrettably no metastable



The usual α-cleavage ions are also present in the spectrum.

Figure 6. Fragmentation scheme for XXXIX



Base peak at m/e 196 (M - t-Bu - n-Pr).

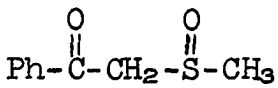
Figure 7. Fragmentation scheme for XL

ions are found in the spectrum to indicate which of these processes is occurring.

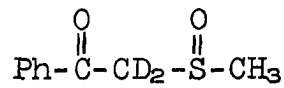
Rearrangements in β-Ketosulfoxides and β-Ketosulfones

Although skeletal rearrangement of organosulfur compounds in the mass spectrometer have been extensively investigated (9,12), the electron impact induced fragmentations of the synthetically important β-ketosulfoxides (90,91, 92,93,94) and β-ketosulfones (95,96) have not been studied.

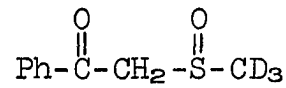
The spectra of ω-(methylsulfinyl)acetophenone (XLIa) and its labelled counterparts (XLIb and XLIc) are given in Table 8. Table 9 contains metastable ions observed in the spectrum of XLIa. Appropriate shifts in the positions of these metastables occur in the spectra of XLIb and XLIc.



XLIa



XLIb



XLIc

Of all the transitions listed in Table 9, only the 182 (M^+) → 105 and the subsequent 105 → 77 processes are due to simple bond cleavage. The m/e 105 ion is the benzoyl cation, formed by cleavage alpha to the carbonyl group. Cleavage between the phenyl ring and the carbonyl group would give another m/e 105 ion, XLII. The spectra of the labelled compounds show no shift of the m/e 105 ion to higher values, ruling out this process. A contribution to

Table 8. Mass spectra of XLIa, XLIb, and XLIc

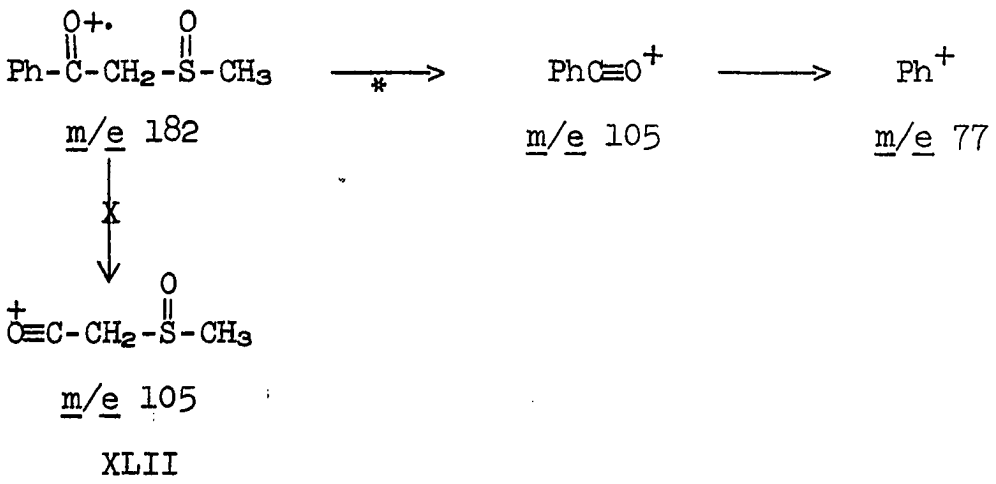
	Relative Intensity[a,b]		
m/e	XLIa	XLIb	XLIc
185			15
184		14	
183		4	
182	24	<1	
169		1	
168			7
167		5	1
166		2	
165	8		
150	1	1	1
122		52	
121		21	47
120	90	5	3
105	100	100	100
93		37	

[a]Spectra taken at 70 ev.

[b]Calculations of the isotopic purity of the molecular ions of XLIb and XLIc are reported in the Experimental section. The calculations were made by the method of Biemann (97) from low voltage spectra.

Table 8 (Continued)

m/e	XLIa	XLIb	XLIc
92		13	
91	54	4	53
77	69	53	57
67		6	
66		7	8
65	16	6	18
64		3	18
63	12	19	
62		5	
61	17		
51	33	30	35



XLII

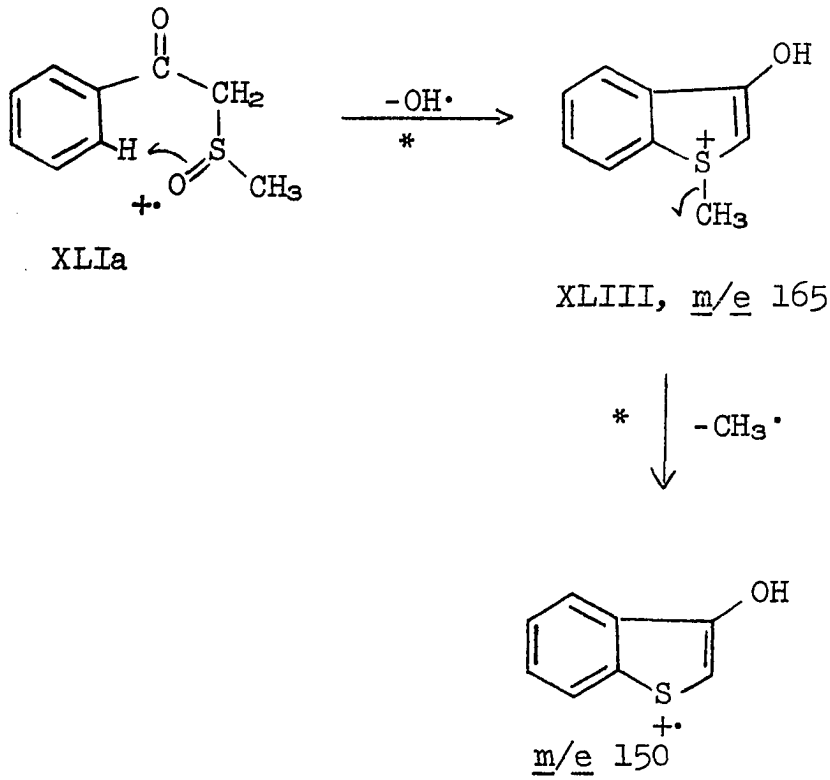
Table 9. Metastable transitions in the spectrum of XLIa

m*	transition
149.6	182 → 165
79.1	182 → 120
60.5	182 → 105
136.3	165 → 150
91.9	120 → 105
69.0	120 → 91
56.5	105 → 77
46.4	91 → 65

the m/e 77 ion by $CH_3SOCH_2^+$ is also excluded by the labelling data.

The loss of OH from the molecular ion (182 → 165 in XLIa) is not unique to this class of sulfoxides. This process also occurs in the spectra of dimethylsulfoxide (56) and styryl sulfoxide (vide supra). The mechanism of OH loss from XLI appears to differ from the mechanism in these compounds, however, since the hydrogen lost as OH comes mainly from the aromatic ring. The ion intensities of Table 8 show that M-17 (OH) predominates over M-18 (OD) in XLIb and XLIc, indicating that the aliphatic hydrogens are lost as OH to only a small extent. The writing of ion structures

for such a rearrangement is probably futile, but an attractive possibility is that the product of the M-17 process is the benzothiophene ion, XLIII. The observed metastable loss



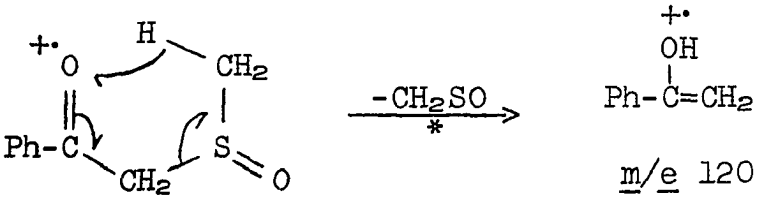
XLIa

XLIII, m/e 165

m/e 150

of $CH_3\cdot$ from this ion strengthens the case for XLIII, expecially since $CD_3\cdot$ is cleanly lost from the m/e 168 ion of XLIc (Table 8).

The formation of the m/e 120 ion by a one-step loss of 62 mass units represents the most interesting process in the spectrum of XLIa. This ion contains no sulfur (determined by the ratio of 120/122) and appears to be formed by hydrogen transfer to the carbonyl oxygen and concomitant loss of thioformaldehyde S-oxide, XLIV.

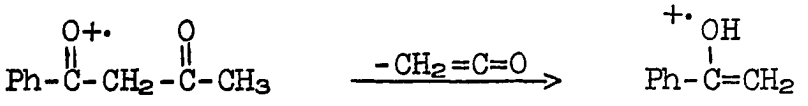


$CH_2=S=O$

XLIV

This process is an example of the McLafferty rearrangement (5); γ-hydrogen transfer to an ionized multiple bond and loss of a stable neutral species.

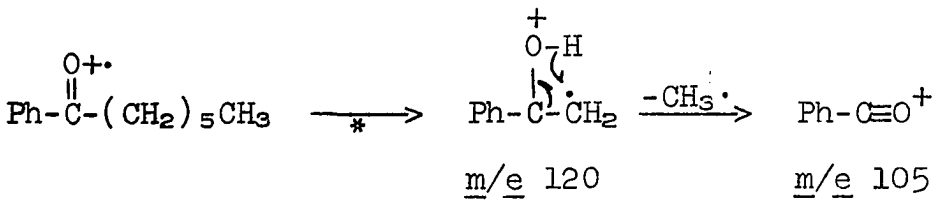
The rearrangement is analogous to the loss of ketene from the molecular ion of benzoylacetone, XLV (98).



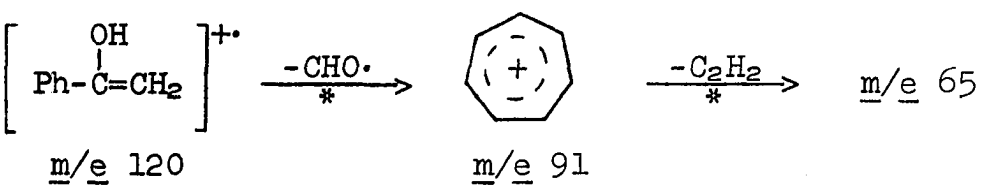
XLV

The m/e 120 ion is shifted to m/e 121 in XLIb and m/e 122 in XLIc as expected for γ-hydrogen transfer and formation of the acetophenone enol ion.

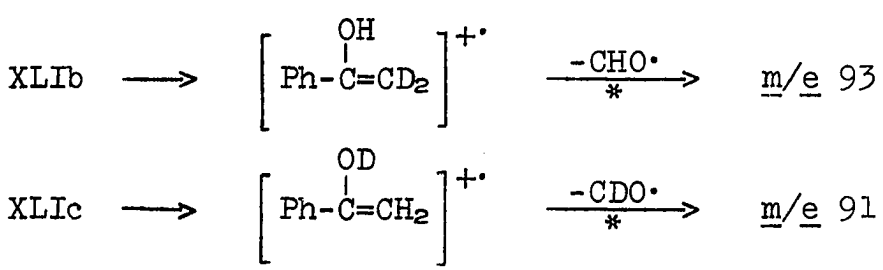
It has been demonstrated that the product ions of McLafferty rearrangement in ketones are in the enolic rather than the keto form (3,99). The one-step loss of 15 mass units from m/e 120 would seem to be incompatible with an enolic structure. Meyerson and Rylander (100), however, have advanced a mechanism for $CH_3\cdot$ loss from the enol which does not require reversion to the keto ion.



Another curious decomposition mode of the m/e 120 ion is the one-step loss of 29 mass units to form the m/e 91 ion. The fragment lost is almost certainly CHO· since the m/e 91 ion loses C_2H_2 (m*) to give the m/e 65 ion. This process is characteristic of the tropylium ion (3, chapter 2). The



120 → 91 process is quite specific. XLIb loses CHO· to give the m/e 93 ion and CDO· is lost from m/e 121 to give m/e 91 in the spectrum of XLIc. Unfortunately, the presence



of interfering peaks prevents the evaluation of label retention in the tropylium minus acetylene ion.

The tropylium ion was also present in the spectrum of benzoylacetone, XLV. A shift of the m/e 91 ion to m/e 93 was observed when the methylene protons were replaced with deuterium (98).

The m/e 120 → m/e 91 process is all the more remarkable since the acetophenone enol ion derived from hexyl phenyl ketone does not fragment to tropylium ion (100). Furthermore, the molecular ion of acetophenone does not fragment in this manner either (100). So the possible reversion of a portion of the enolic ion to the keto form is not responsible for the 120 → 91 process.

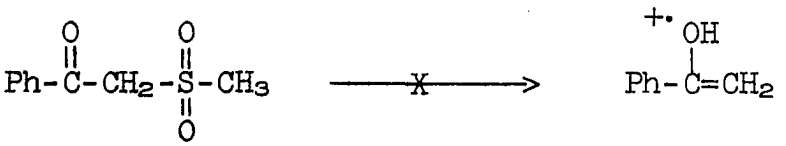
The neutral fragment, XLIV, ejected from the molecular ion to form the m/e 120 ion is the simplest sulfine, thioformaldehyde S-oxide. There is no ion at m/e 62, indicating that charge is retained solely on the acetophenone enol. The ions at m/e 61 and m/e 63 are of unknown structure.

A rearranged ion of methyl phenyl sulfone apparently expels XLIV (56), although the evidence is not as compelling as the labelling results obtained in this work. Sulfines more complex than XLIV have been prepared chemically and some are reasonably stable (101 and references contained therein).

Sulfenes ($R_2C{=}SO_2$) are less stable than sulfines and no sulfene has been isolated, although their existence as intermediates has been suggested for several reactions (101).

The availability of β-ketosulfoxides and β-ketosulfones presented an excellent opportunity to test the theory that the stability of the expelled neutral fragment controls the rate of ion rearrangement (10).

McLafferty rearrangement in ω-(methylsulfonyl)acetophenone, XLVI, would result in expulsion of thioformaldehyde S,S-dioxide, XLVII, the simplest sulfene. As evidenced by



XLVI

m/e 120

$CH_2=SO_2$

XLVII

the lack of an m/e 120 ion in the spectrum (Table 10), sulfene loss does not occur. Nor does the process occur with retention of charge on the sulfene, since no ion appears at m/e 78.

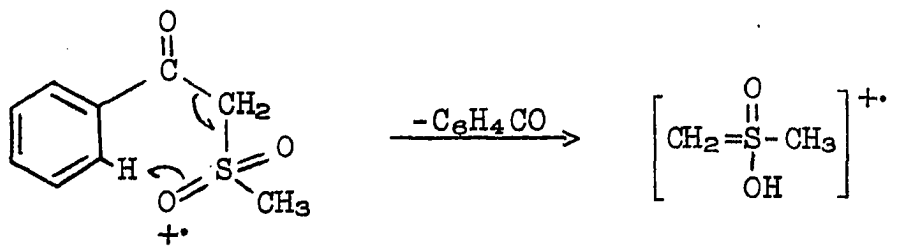
Table 10. Mass spectrum of XLVI

m/e	Relative Intensity
198 (M^+)	23.1
105	100.0
94	8.1
91	10.0

Table 10 (Continued)

m/e	Relative Intensity
77	37.6
65	7.6
63	3.3
51	16.7

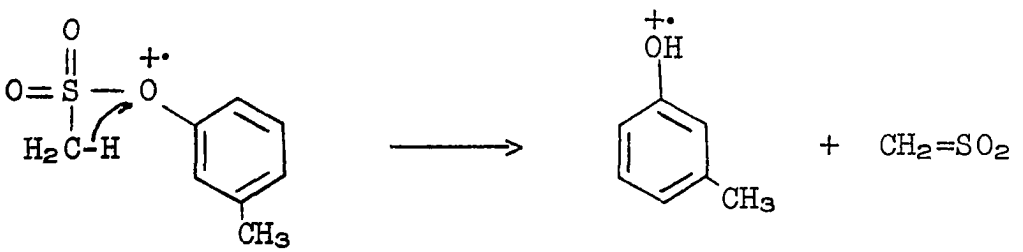
The presence of an m/e 91 ion in the spectrum of XLVI is somewhat surprising since the ion was formed from the m/e 120 ion of the β-ketosulfoxide. No metastable ion exists in the spectrum of XLVI to designate the precursor of the m/e 91 ion, but the presence of a metastable ion at m/e 46.4 (91 → 65) is strong evidence that it has the tropylium ion structure. The m/e 94 ion probably has the elemental composition of dimethylsulfone ($C_2H_6SO_2$). Its formation can be visualized as abstraction of hydrogen from the benzene ring followed by (or concomitant with) cleavage.



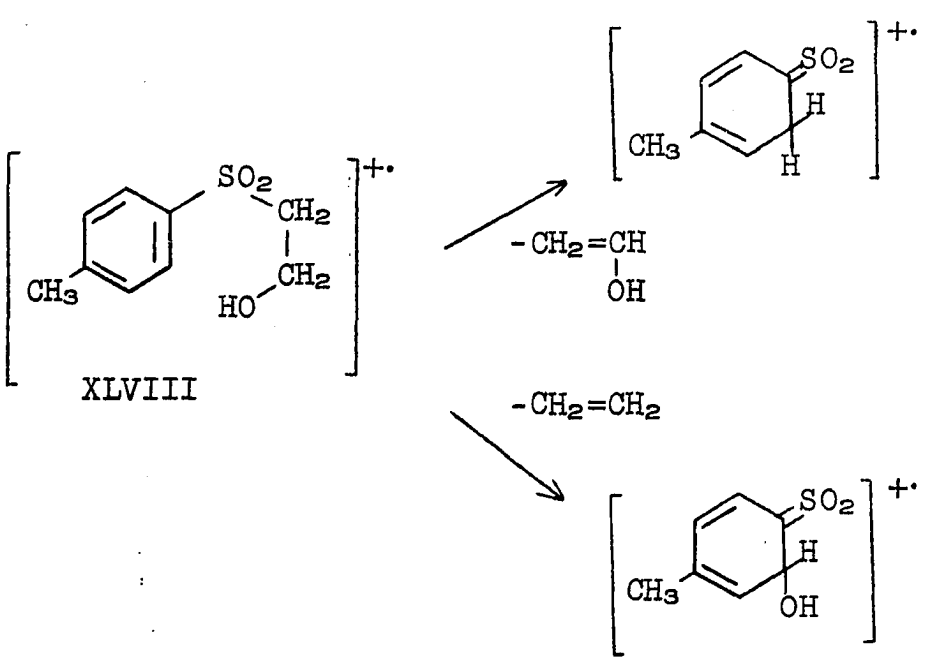
XLVI

m/e 94

The loss of CH_2SO_2 from the molecular ion occurs in the spectrum of aromatic methyl sulfonates, but the absence of a metastable ion or labelling data weakens the case for the proposed sulfene expulsion (102).

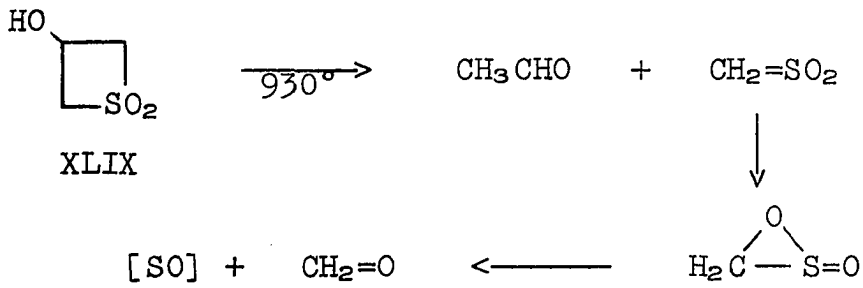


Sulfenes have been suggested as the structure of the ions derived from acetaldehyde and ethylene rejection from the molecular ion of XLVIII (103). No evidence was produced to support these structures.



XLVIII

Thioformaldehyde S,S-dioxide, XLVIII, is formed in the pyrolysis of XLIX at 930° (104). It cannot be observed directly but the presence of formaldehyde and sulfur monoxide polymer are indications of its transient existence.

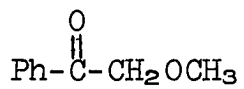


XLIX

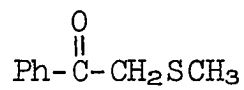
It was hoped that the β-ketosulfone, XLVI, could be induced to lose CH_2SO_2 in the high temperature inlet system of the mass spectrometer. A small m/e 120 ion was formed at ca. 200° but there is no real information about its origin or structure. Raising the temperature to ca. 300° caused almost total disintegration of the molecule and formation of peaks at practically every mass below the molecular ion.

Failure of the β-ketosulfone to lose a sulfene molecule strengthens the theory that stability of the expelled neutral fragment helps control the extent of rearrangement (10).

To further test this theory, the β-ketoether (L) and β-ketothioether (LI) were prepared. McLafferty rearrangement would result in expulsion of formaldehyde and thio-



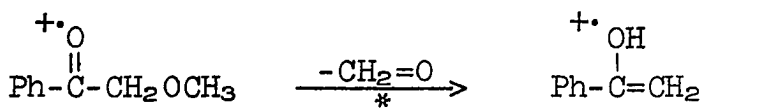
L



LI

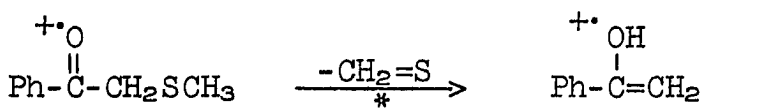
formaldehyde, respectively, from these molecules. Other workers have found that thioformaldehyde is less readily expelled than formaldehyde from similar molecules (105,106, 107). This is not surprising in view of the instability of organic molecules containing doubly-bonded sulfur (108).

A comparison of the spectra (Table 11) of L and LI shows that formaldehyde expulsion occurs ca. 330 times as readily as expulsion of thioformaldehyde, based on the ratio of $120/M^{+}$.



m/e 150 (1.2) m/e 120 (51.2)

L



m/e 166 (38.1) m/e 120 (4.8)

LI

Except for the peak at m/e 61 (probably $CH_2=\overset{+}{S}-CH_3$) in LI, the spectra are remarkably similar below m/e 105. The

Table 11. Mass spectra of L and LI

m/e	Relative Intensity L[a]	LI[b]
166		38.1
150	1.2	
120	51.2	4.8
105	100.0	100.0
91	5.6	5.7
77	50.0	47.7
65	3.1	6.2
63	1.7	2.9
61		10.5
51	20.7	21.0
50	7.1	7.1

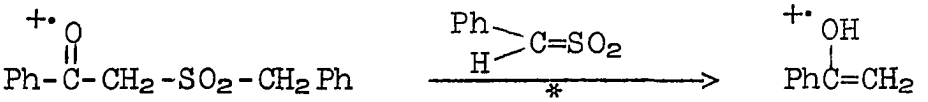
[a]Metastable ions observed for 150→120, 105→77, 91→65.

[b]Metastable ions observed for 166→120, 166→105, 105→77.

tropylium ion (m/e 91) is present in the spectra of these compounds, as it is in the β-ketosulfoxide and β-ketosulfone spectra. It probably does not occur exclusively by loss of CHO· from the m/e 120 ion since the intensities of m/e 91 are virtually the same in the two compounds while the m/e

120 ion is much stronger in L than in LI. This assumption may be unwarranted since equating the intensity of an ion with its importance in subsequent fragmentation is not always justified (109). No metastable ion for the formation of m/e 91 appears in these spectra.

ω-(Benzylsulfonyl)acetophenone, LII, was prepared in order to determine whether sulfene loss can occur when the sulfene is stabilized by a phenyl ring. It was gratifying to observe an m/e 120 ion in the spectrum (Table 12) of LII, although the ion was of low intensity. A metastable ion at m/e 52.6 confirmed that thiobenzaldehyde S,S-dioxide was lost from the molecular ion in one step.



m/e 274 (5.0) LII

m/e 120 (1.7)

The major ions in the spectrum of LII were due to α-cleavage at the carbonyl group to give the benzoyl cation (m/e 105) and at the sulfinyl group to give the tropylium ion (m/e 91). The small ion at m/e 209 ($274 \xrightarrow{*} 209$) is probably due to loss of $SO_2H\cdot$ from the center of the molecule. There are a number of other ions of unknown elemental composition and structure in the spectrum.

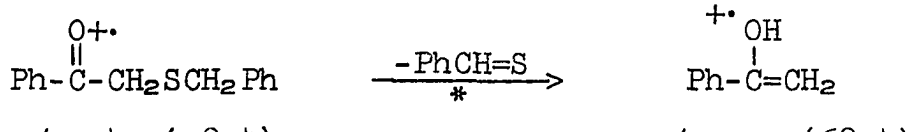
Table 12. Mass spectra of LII, LIII, and LIV

m/e	Relative Intensity LII	LIII	LIV
274	5.0		
258			5.2
242		28.4	
224		1.2	
209	1.0		
199	1.0		
189			1.9
173			2.7
148	1.2		
145			1.9
124			1.5
120	1.7	68.4	1.5
105	44.3	100.0	13.3
91	100.0	50.8	100.0
89	2.9		
86	6.4		
85	7.4		4.8
83	10.5		7.3
77	9.5	39.0	13.1
65	17.4	12.2	9.4

Table 12 (Continued)

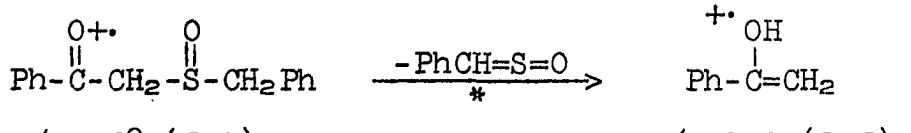
m/e	LII	LIII	LIV
63	3.8	2.8	2.1
57	7.2		3.5
56	3.3		
51	8.3	12.6	6.7

The spectrum (Table 12) of the corresponding β-keto-sulfide, LIII, exhibited a large m/e 120 ion with a metastable ion for the 274 → 120 process. Thiobenzaldehyde is apparently highly stable relative to thioformaldehyde, as expected. The corresponding sulfine, thiobenzaldehyde S-oxide, does not seem to derive as much stabilization from the phenyl group as the corresponding thioaldehyde and sulfene. The m/e 120 ion in LIV is of low intensity, although a metastable ion for the 258 → 120 process is observed.



m/e 242 (28.4) m/e 120 (68.4)

LIII



m/e 258 (5.2) m/e 120 (1.5)

LIV

The spectrum of LII (Table 12) contains a perplexing ion at m/e 224. A metastable ion indicates it is formed from the molecular ion, m/e 242, in one step. These 18 mass units must consist of H_2O. Water is commonly lost from molecules containing an OH function and even from aliphatic sulfoxides (3), but the loss of the oxygen from the carbonyl function as water is rather unusual, although not unprecedented (3). Any attempt to rationalize a mechanism or structure for the m/e 224 ion would be futile without further information.

The prospect of competitive elimination of ethylene and the sulfine, XLIV, led to the examination of the spectrum of LV, Table 13.

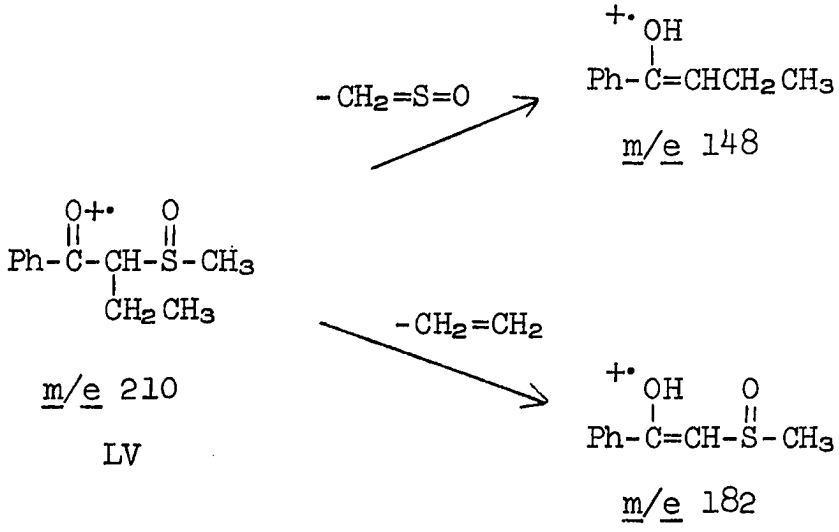


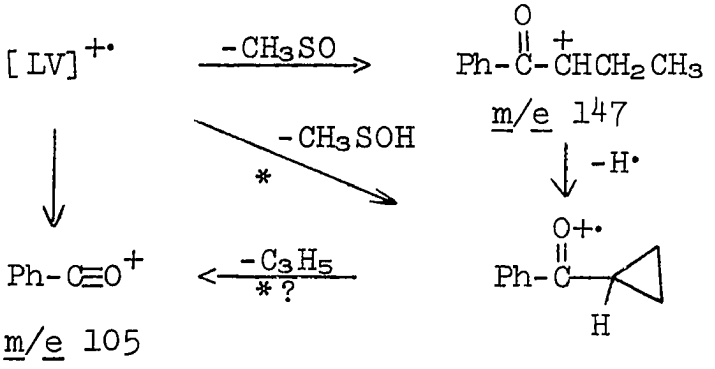
Table 13. Mass spectra of LV and LVI

m/e	Relative Intensity LV	LVI
226		3
210	6	
198		10
182	1	
147	20	7
146	7	9
105	100	100
91	7	2
89	5	
77	42	32
69	5	2
65		1
64	1	
63	1	1

Neither of these processes occurred to any significant extent. A small peak at M-28 is observed, but the M-62 ion is absent.

The predominant process is simple cleavage to give the benzoyl ion (m/e 105). Cleavage alpha to the sulfoxide group

also occurs to give an ion at m/e 147 (M-CH_3SO). This ion is apparently an α-keto carbonium ion, which can lose a hydrogen atom to give the ion at m/e 146, represented as cyclopropyl phenyl ketone. This ion is also formed by the one-step loss of CH_3SOH from the molecular ion. A possible



metastable ion at m/e 76.5 for the 146 → 105 process is so obscured by the m/e 77 ion that its existence is rendered uncertain.

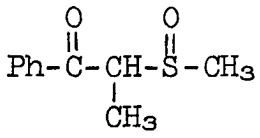
The β-ketosulfone, LVI, undergoes essentially the same fragmentations in the mass spectrometer as the sulfoxide, Table 13. Loss of CH_3SO_2 from the molecular ion gives the ion at m/e 147. The ion at m/e 146 can be formed by hydrogen loss from m/e 147 or the one-step loss of CH_3SOH from the molecular ion (m* observed).

Sulfine loss from the molecular ion is observed in the spectrum of LVII, Table 14. α-Cleavage to give the α-keto-carbonium ion still occurs, although the M-CH_3SOH process is

Table 14. Mass spectra of LVII and LVIII

m/e	Relative Intensity LVII[a]	LVIII
212		14
196	22	
179	1	
147	6	
134	16	
133	38	1
119	5	
105	100	100
91	5	<1
89	1	<1
79		2
77	52	30
75	13	
69	1	
64	3	
63	4	

[a]Metastable ions were observed for 196→134, 196→133, 133→105, 105→77.



LVII

eliminated. The molecular ion of LVII is probably unable to attain a conformation that allows OH bonding and loss of CH_3SOH. The ethyl groups of LV and LVI, on the other hand, provide hydrogens for easy formation of the OH bond and CH_3SOH loss does occur.

The fragmentation pattern of LVII is outlined in Figure 8. The origin and structure of the ions at m/e 75 and m/e 69 are unknown. The ions at m/e 63 and m/e 64 are probably CH_3SO^+ and CH_3SOH^+, respectively. The $133 \xrightarrow{*} 89$ process is intriguing, but speculation as to the fragment lost and the structure of the m/e 89 ion is futile without high-resolution data on the elemental composition.

This process also occurs in the spectrum, Table 14, of the corresponding β-ketosulfone, LVIII. Otherwise the spectrum of LVIII is unremarkable.

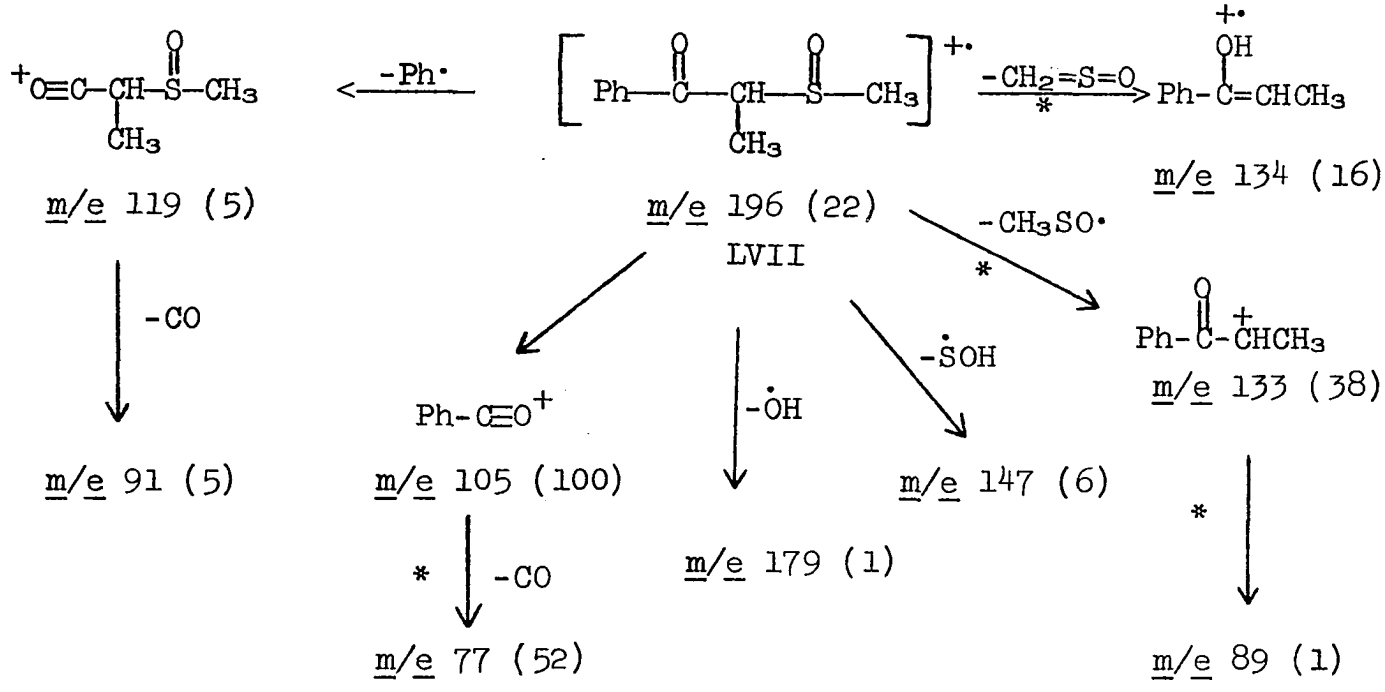
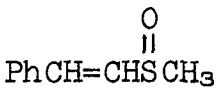


Figure 8. Fragmentation scheme for LVII

Rearrangements in Unsaturated Sulfoxides and Sulfones

The spectrum of methyl vinyl sulfoxide, LIX, was examined chiefly for evidence of styryl migration from sulfur to oxygen. A similar rearrangement, which presumably



LIX

forms a sulfenate ion, had previously been observed in aromatic sulfoxides and it was suggested that the orbitals of the aromatic group were interacting with the electron deficiency localized on the oxygen atom (54). We felt that the orbitals on the olefinic double bond of LIX would behave similarly and styryl migration would occur. Vinyl group migration was very recently shown to occur in methyl vinyl sulfoxide (66).

The spectrum of LIX is given at 70 ev and 14 ev in Table 15. The compound yields a large number of ions. Many are of unknown origin and structure, but a great deal of mechanistic information can be derived from the spectrum.

The item of paramount interest, styryl migration to oxygen, is easily detected by observation of the metastable loss of $CH_3S\cdot$ to give an ion at m/e 119. The sulfenate ion, LX, is presumably the precursor of the m/e 119 ion. A possible alternative structure, LXI, is ruled out by the

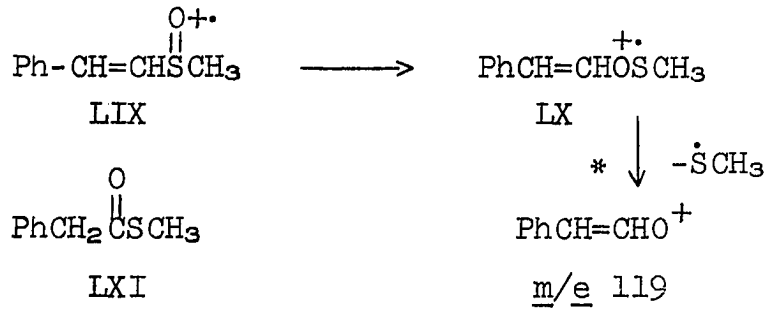
Table 15. Mass spectrum of LIX

m/e	Relative Intensity 70 ev	14 ev
166 (M^+)	100	100
151	31	6
150	12	
149	4	
138	42	31
137	59	28
135	12	
134	21	
133	25	
123	57	
119	42	17
118	34	
117	9	
107	26	
103	73	9
102	40	
91	93	2
90	8	
89	11	
79	16	

Table 15 (Continued)

m/e	70 ev	14 ev
77	77	
65	10	
64	13	
63	18	
51	54	
50	20	

major differences in its spectrum, Table 16, and the spectrum of LIX.



The structure drawn for the product of the M-SCH_3 process is obviously energetically unfavorable since the oxygen has only six electrons. A canonical form of the ion is certainly more stable, but one fragmentation route of the ion seems to require form A.

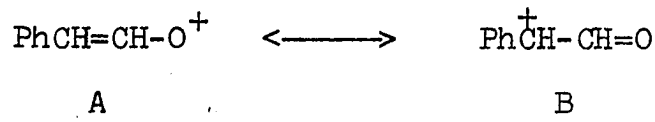


Table 16. Mass spectrum of LXI

m/e	Relative Intensity
166 (M^+)	41
138	1
119	13
91	100
75	4
65	13

One fragmentation route of this ion involves hydrogen (or hydride) migration to the carbon atom alpha to the phenyl ring to yield the phenyl acylium ion. A one-step loss of CO from this ion is observed as expected.

$$PhCH_2C{\equiv}O^+ \xrightarrow[*]{-CO}$$ 

m/e 91

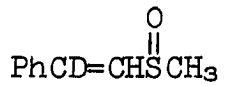
Another fragmentation mode of the m/e 119 ion is loss of hydrogen to give an ion at m/e 118. A possible metastable ion for this process is very weak and cannot be assigned with certainty. The m/e 118 ion could also result from SO loss from the molecular ion, a common process in

some sulfoxides (55,56). High resolution data[a] for this compound demonstrated that SO loss from the molecular ion does not occur. The spectra of the labelled compounds (vide infra) confirmed the high resolution data.

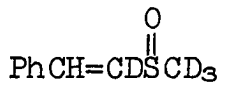
The structure of the m/e 118 ion is a matter of considerable interest. Hydrogen loss from the m/e 119 ion could produce the phenyl ketene radical ion. That this

$$\underline{m/e}\ 119 \xrightarrow{-H\cdot} PhCH{=}C{=}O^{+\cdot}\ (\underline{m/e}\ 118)$$

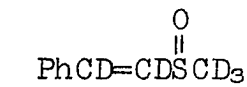
process does not occur was demonstrated by the spectra (Table 17) of the labelled compounds, LXII, LXIII, and LXIV. It is clear that the hydrogen lost from the m/e 119 ion comes from the aromatic ring.



LXII



LXIII



LXIV

It is proposed that electrophilic attack upon the benzene ring by the positive oxygen atom forms a protonated benzofuran ion. Loss of a hydrogen from the benzene ring yields the molecular ion of benzofuran.

---

[a]Obtained by J. R. Althaus, Massachusetts Institute of Technology, Boston, Mass.

Table 17. Mass spectra of LXII, LXIII, and LXIV[a]

m/e	Relative Intensity LXII	LXIII	LXIV
171			87
170		72	8
169		11	
167	56		
155			12
154		11	5
153			26
152	21	22	5
151	13		
150	3		
143			30
142		30	8
141		9	52
140		46	
139	58		
138	44		
137			19
136	13	13	16

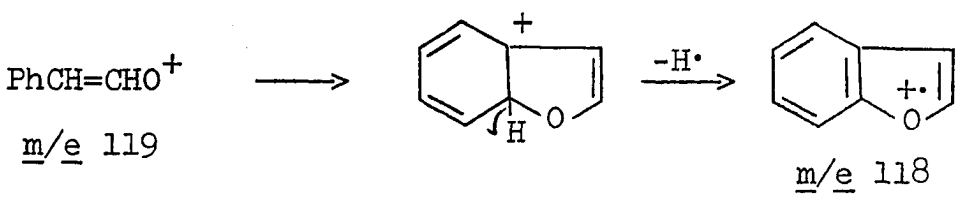
[a]Low ev spectral determinations of isotopic labelling are in the Experimental section.

Table 17 (Continued)

m/e	LXII	LXIII	LXIV
135	17	20	20
134	20	20	8
133	6		
125			43
124	54	44	35
123			10
122			14
121			42
120	31	37	32
119	30	28	8
118	8		
109			26
108	22	22	
106			18
105			56
104	40	59	18
103	22	35	23
102	18		
93			100
92	100	100	
91	13		

Table 17 (Continued)

m/e	LXII	LXIII	LXIV
90	11		
80	19	17	
79			31
78	76	41	39
77	77	48	37



m/e 118

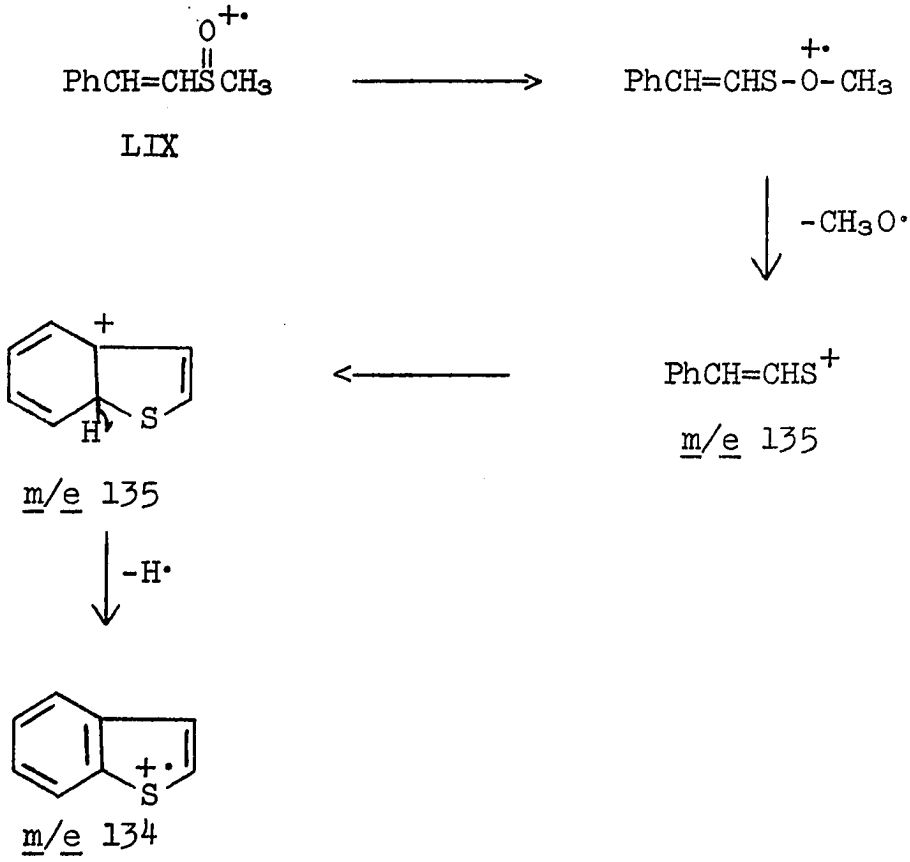
Benzofuran loses CO from the molecular ion (3) to give an m/e 90 ion and a peak at m/e 90 is observed in the spectrum of LIX. This ion could also result in part from loss of CHO· from m/e 119.

Electrophilic substitution in an electron impact induced ion is not a novel process, but has been observed a number of times with oxygen (6,110,111,112,113) and sulfur (114,115) as the attacking species.

The route to the tropylium ion from m/e 119 appears to have a lower activation energy (or higher frequency factor)

than the route to benzofuran ion, as indicated by the ca. 3:1 ratio of the abundances of m/e 91 to m/e 118. Also, at 14 ev the 119 → 91 process still occurs while the m/e 118 ion has disappeared.

Recent work (65,66) has indicated that methyl groups attached to sulfoxide may migrate to oxygen in an electron impact induced ion. No metastable ions are observed for loss of $CH_3O\cdot$ from a sulfenate resulting from methyl migration, although the spectrum of LIX contains ions at m/e 135 and 134 which could result from such processes. The low intensities of these peaks precludes observation of fragment ions derived from them.



Two processes which must be complex, yet are very important, are losses of CO and/or CHO· from the molecular ion of LIX in one step to give abundant ions at m/e 138 and 137. The CHO· appears to originate from one of the carbon atoms bonded to the sulfoxide function. LXII loses no CDO· while LXIII (and LXIV) loses CDO· predominantly. The small amount of M-29 ion in LXIII and LXIV may, in fact, be the result of hydrogen loss from the M-CO ion.

Neither CO nor CHO· loss from the molecular ion is observed in the spectrum of LXV, Table 18. CO is lost from the M-CH_3· ion of this compound and also from the M-CH_3· ion of LIX. A metastable ion is also seen for the loss of CH_3CO· from the molecular ion of LXV. This data would seem to confirm that both CO and CHO· loss involves the vinyl carbon alpha to the sulfoxide group. The fragmentation schemes of LIX and LXV are illustrative of most of the fragmentations of these sulfoxides, Figures 9 and 10. Depicting certain processes as occurring from the unrearranged ion and others from the sulfenate ion is arbitrary with no evidence for the correctness of the scheme. The only process which must occur from the sulfenate ion is loss of SCH_3.

Table 18. Mass spectrum of LXV

m/e	Relative Intensity
180 (M^+)	44
165	9
164	4
163	3
150	7
137	81
133	19
132	13
117	76
116	43
115	100
105	24
91	49
89	14
77	14
65	16
51	22

The origin of hydrogen lost as OH (m*) from the molecular ion of these compounds cannot be determined with deuterium labelling because of peaks which interfere with the weak M-OH ion. The process becomes important in LXVI

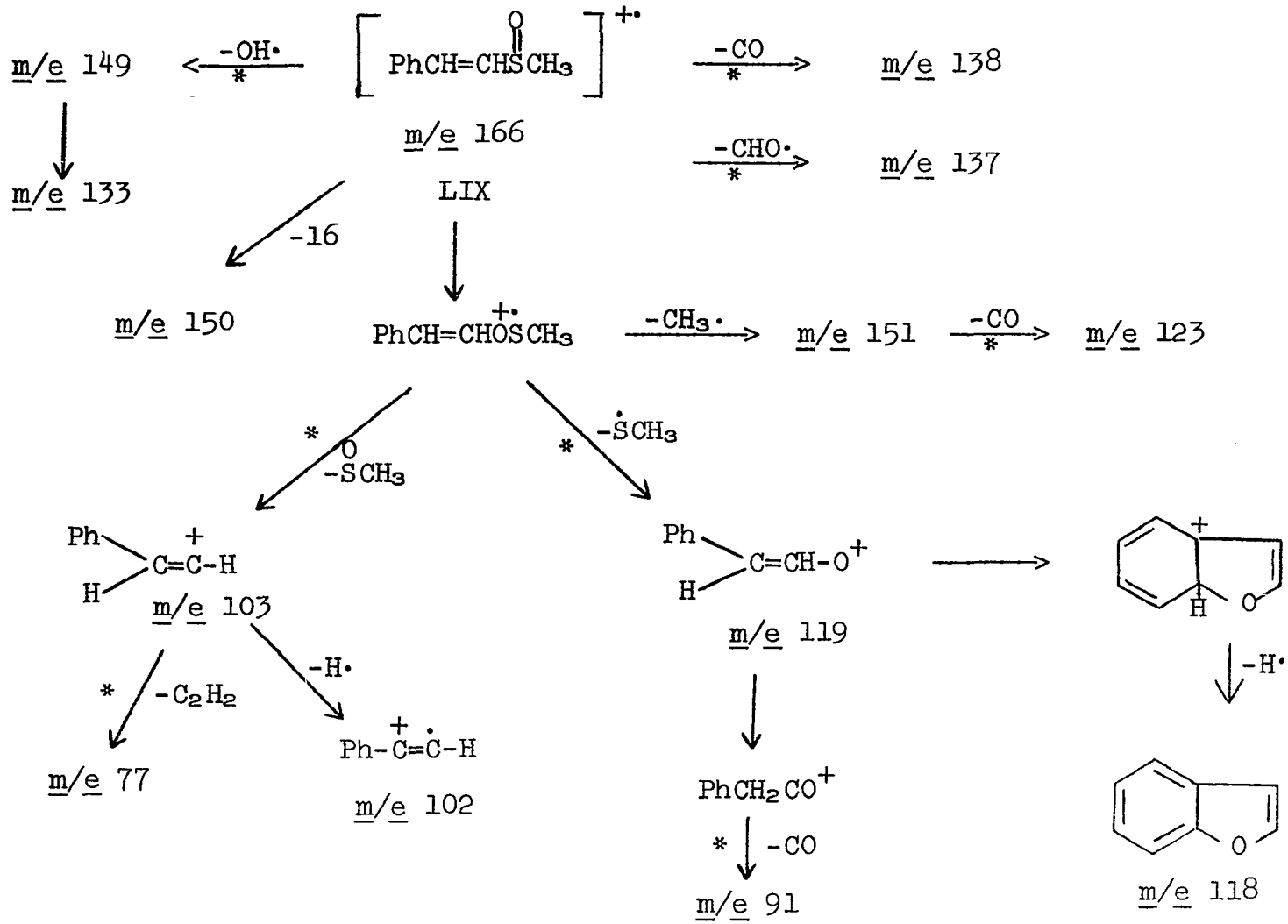


Figure 9. Fragmentation scheme for LIX

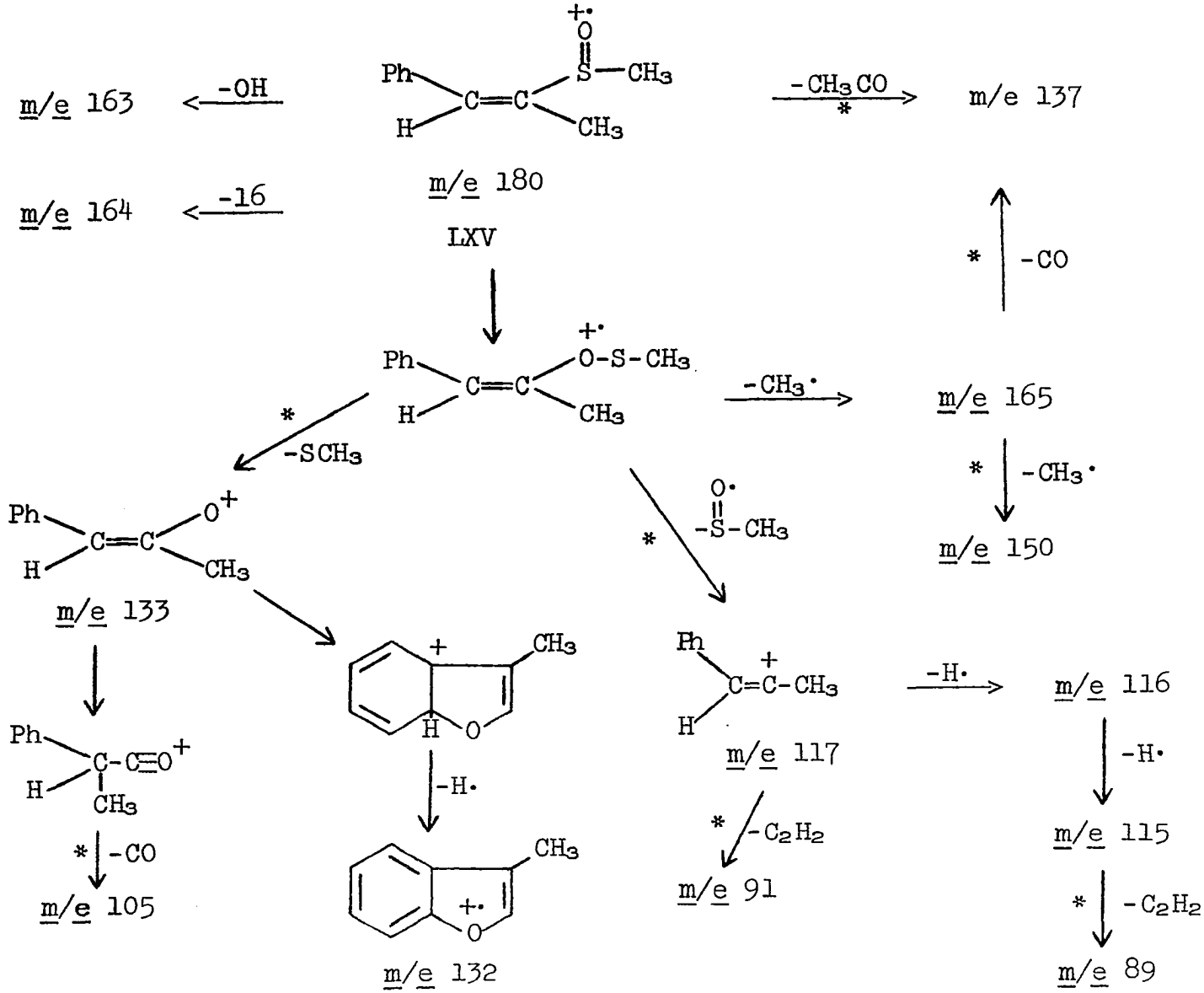
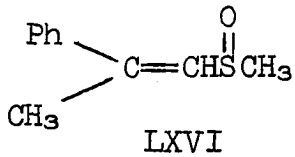
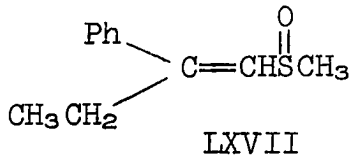


Figure 10. Fragmentation scheme for LXV

and LXVII, presumably because oxygen can more easily abstract the hydrogens of the methyl (LXVI) and ethyl (LXVII) groups, Table 19.



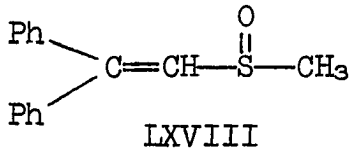
LXVI



LXVII

The one-step loss of 16 mass units (CH_4?) from the M-OH ion is beyond rational explanation, especially since the structure of the M-OH ion is unknown.

The sulfoxide-sulfenate rearrangement is especially favorable in LXVIII. The M-SCH_3 ion (m/e 195) is the base



LXVIII

peak in the spectrum, Table 20. As usual, this ion fragments both by loss of CO and loss of H.

A facile cleavage occurs in all of these sulfoxides to yield vinyl carbonium ions which may fragment in various ways, Figures 9 and 10. A product of this fragmentation, the indenyl cation (m/e 115), is the base peak in the spectra of LXV and LXVI.

Aromatic sulfones undergo sulfone-sulfinate rearrangement by migration of an aryl group (54). Methyl styryl sulfone, LXIX, was prepared in order to determine if styryl

Table 19. Mass spectra of LXVI and LXVII

m/e	Relative Intensity LXVI	LXVII
194		44
180	47	
179		19
178		15
177		77
166		6
165	23	5
164	8	
163	19	6
162		10
161		29
152	15	
151	17	5
150	14	
147	28	21
137	18	6
135	14	28
134	18	7
133	55	4
132	25	

Table 19 (Continued)

m/e	LXVI	LXVII
131	11	14
130		16
129		49
128		41
127		12
117	22	14
116	22	21
115	100	40
105	65	8
103	24	15
102	14	17
91	72	100
89	20	9
79	12	8
78	11	6
77	39	27
65	24	14
63	30	12
59	22	
51	40	23
50	16	9

Table 20. Mass spectrum of LXVIII

m/e	Relative Intensity
242 (M^+)	33
227	40
226	5
225	1
199	10
195	100
194	24
178	44
177	11
176	12
167	44
165	35
152	15
134	12
77	14
51	15

group migration from sulfur to oxygen would occur.

$PhCH{=}{=}CHSO_2CH_3$

LXIX

The spectrum of LXIX is given in Table 21 and Figure 11 contains the fragmentation scheme.

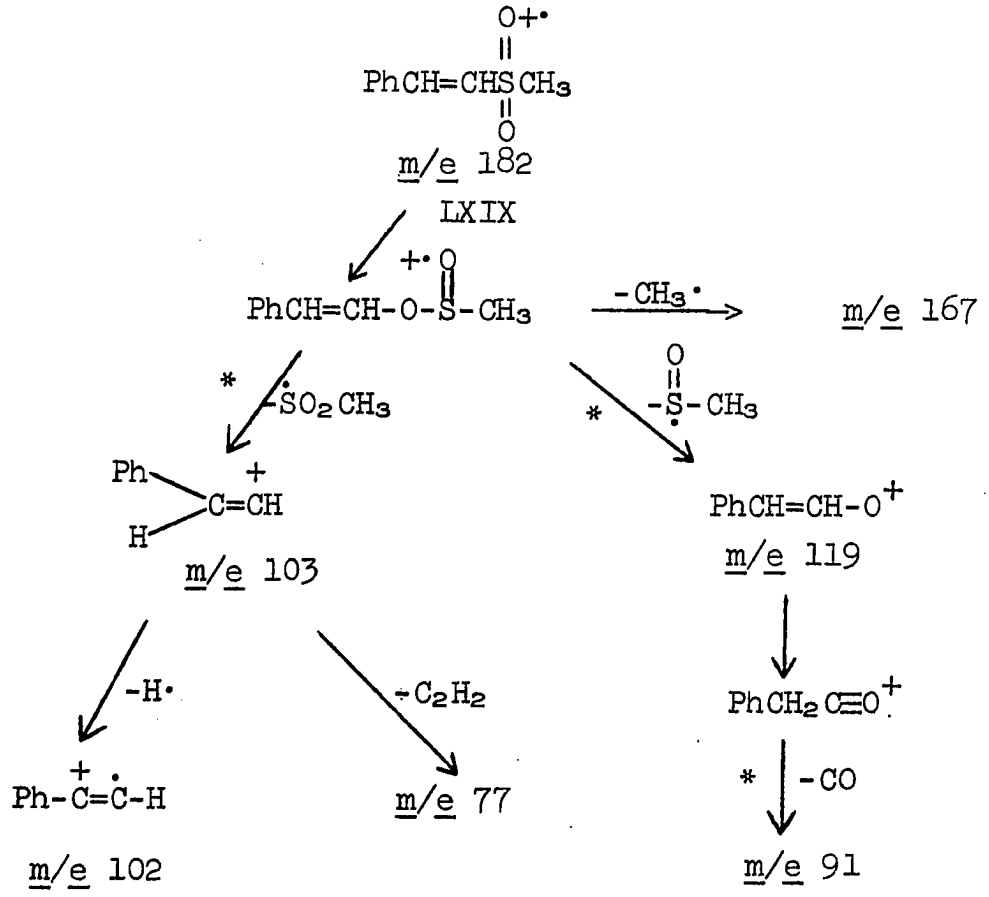


Figure 11. Fragmentation scheme for LXIX

Table 21. Mass spectrum of LXIX

m/e	Relative Intensity
182 (M^+)	20
162	3
119	8
103	46
102	100
91	26
77	31
65	4
63	5
51	18
50	6

There are two rather important differences in the fragmentation pattern of this compound and the vinyl sulfoxides.

No CO or CHO· loss from the molecular ion of LXIX is observed. Carbon-oxygen bond formation does occur, as evidenced by loss of CH_3SO· from the (presumably) sulfinate ion.

Another difference is that the m/e 119 ion (M-CH_3SO·) does not behave in the same manner as it does when formed by

an M-$CH_3S\cdot$ process in sulfoxides. No hydrogen is lost to form the m/e 118 ion, although the 119-CO process does occur.

The reason for this behavior is obscure. The m/e 119 ion is presumed to have the same structure, whether it is derived from sulfoxide or sulfone. It may be that the ion derived from sulfone has insufficient energy to effect electrophilic attack upon the benzene ring, causing a subsequent loss of H· from the ring. The 119 → 118 process does require more energy than the 119 → 91 process, as evidenced by the low ev spectra of the sulfoxides. Of course it is possible that the assumption of a common structure for the m/e 119 ion from both sources is naive.

Whatever the reason for the difference in behavior of sulfoxides and sulfones, consistent results are obtained. All of the sulfoxides previously discussed lost hydrogen from the M-$CH_3S\cdot$ ion. Likewise, sulfones LXX and LXXI formed sulfinate ions and subsequently lost $CH_3SO\cdot$, but no hydrogen loss from the M-$CH_3SO\cdot$ ions was observed. Furthermore, no CO or CHO· loss from the molecular ions was observed in the spectra (Table 22) of these two compounds.

$PhCH{=}C(CH_3)SO_2CH_3$ $\qquad$ $Ph_2C{=}CHSO_2CH_3$

LXX $\qquad$ LXXI

Abundant ions resulting from cleavage to give a vinyl cation were present in the spectra of all three of the sulfones.

Table 22. Mass spectra of LXX and LXXI

m/e	Relative Intensity LXX	LXXI
258		71
196	25	
195		14
179		87
178		100
177		23
176		18
167		43
165		16
152		23
151		12
133	9	
117	24	
116	100	
115	43	
105	22	
91	18	
89	8	12
79	6	
77	9	17

Table 22 (Continued)

m/e	LXX	LXXI
65	7	
63	10	
51		20

Several phenyl styryl sulfoxides and sulfones were prepared with the hope of assessing the relative importance of aryl vs. styryl migration.

Figure 12 shows major fragmentation routes for phenyl styryl sulfoxide, LXXII. The spectrum is given in Table 23.

Attachment of the phenyl ring to the sulfoxide group causes a major new fragmentation to predominate. One-step loss of SO occurs to give an ion at m/e 180. This ion can be represented as the stilbene molecular ion since the appearance of the spectrum from m/e 180 to m/e 165 resembles the spectrum of stilbene (3, chapter 1).

The two possible sulfenate ions are both apparently formed to some extent. Loss of PhS· gives the m/e 119 ion (no m/e 118) and loss of PhO· gives the ion at m/e 135 which can lose hydrogen to give the benzothiophene ion at m/e 134. Unfortunately, no metastable ions are in evidence to confirm that these process occur in one step. At low ev the m/e 135

and 134 ions both disappear while the m/e 119 ion is still present.

Table 23. Mass spectrum of LXXII and LXXIII

m/e	Relative Intensity LXXII	LXXIII
244		92
228	11	
212	7	
211	3	
199	3	
180	100	6
179	34	15
178	15	7
165	14	4
135	4	
134	6	
125		19
119	6	34
103	13	66
102	9	92
91	34	100
77	31	68

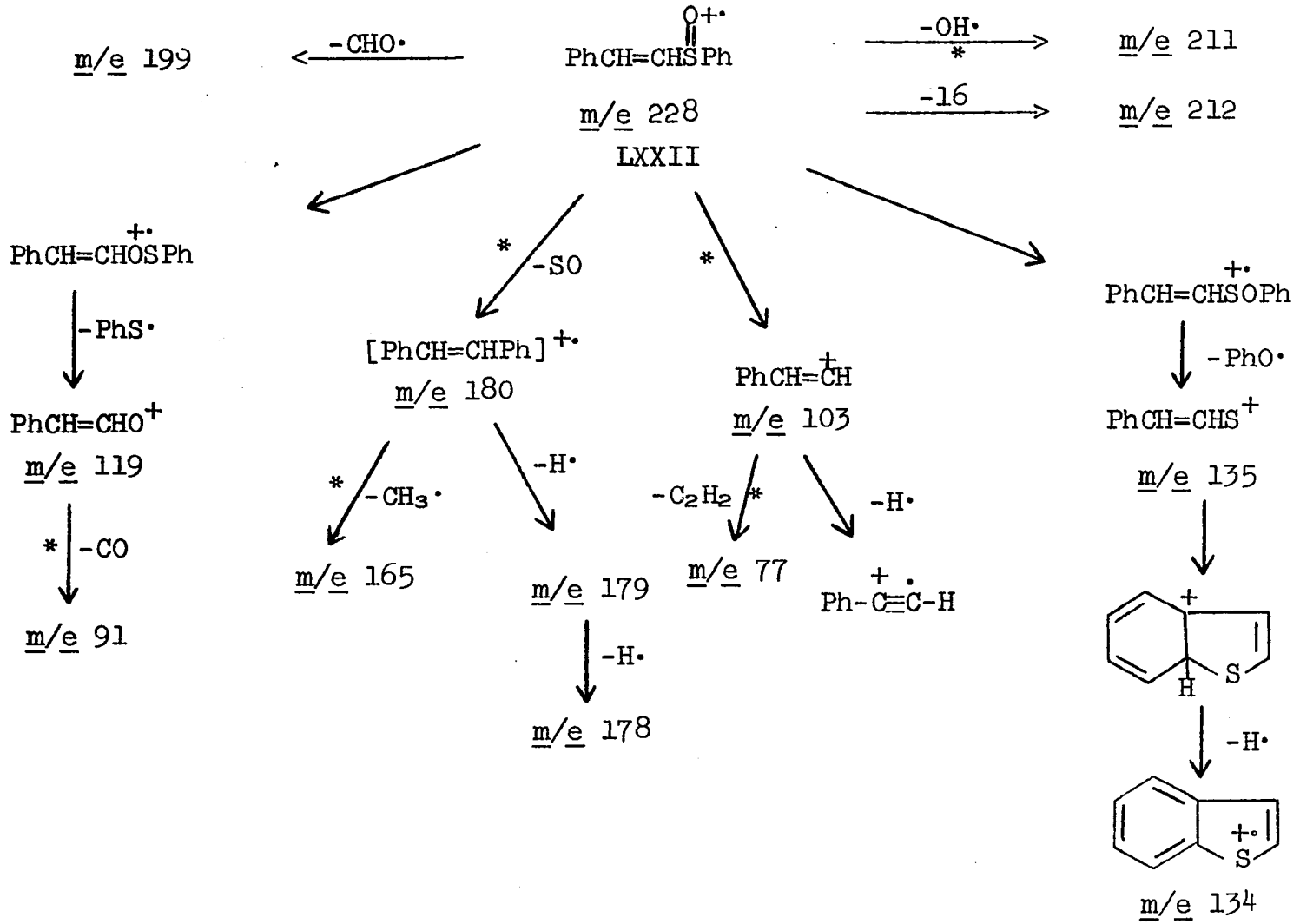
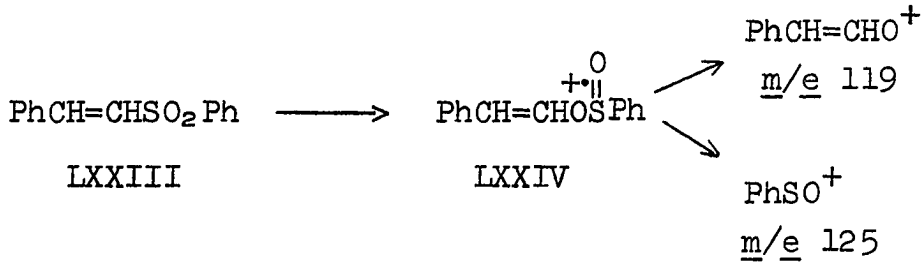


Figure 12. Fragmentation scheme for LXXII

Phenyl styryl sulfone, LXXIII, shows a clear preference for styryl migration at 70 ev. This spectrum is also given in Table 23.

The m/e 119 ion resulting from styryl migration is very abundant in the 20 ev and 16 ev spectra of LXXIII. Furthermore, the ion at m/e 125 results from charge retention on the other fragment from sulfinate LXXIV. No metastable ions



exist for these processes. A metastable ion is observed for the 119 → 91 fragmentation.

No ions derived from phenyl migration are observed in the spectrum. The loss of SO_2 is considerably less important than the loss of SO from LXXII, in agreement with other work (55,56).

The spectra of p-bromophenyl styryl sulfoxide, LXXV, and p-bromophenyl styryl sulfone, LXXVI, also exhibit an m/e 119 ion which predominates over the ions derived from phenyl migration, Table 24. p-Nitrophenyl styryl sulfone, LXXVII, also undergoes styryl migration in preference to phenyl migration, Table 25. The m/e 119 ion is present at low

Table 24. Mass spectra of LXXV and LXXVI

m/e	Relative Intensity LXXV	LXXVI
322		31[a]
306	5[a]	
290	6[a]	
277	11[a]	
258	100[a]	4[a]
203	2[a]	9[a]
179	42	15
178	6	28
155	3[a]	6[a]
135	5	
134	9	
119	12	46
118	4	2
108	11	
103	27	56
102	20	100
91	65	55

[a]Isotope peaks indicate that this ion contains a bromine atom.

Table 24 (Continued)

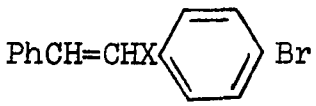
m/e	LXXV	LXXVI
89	15	
77	57	51
76		20
65	9	5
63	10	7

Table 25. Mass spectrum of LXXVII

m/e	Relative Intensity
289 (M^+)	91
201	6
186	4
178	5
139	7
122	6
119	14
103	26
102	99
91	100
77	33
76	10

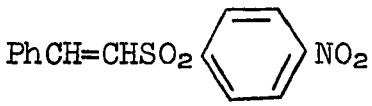
Table 25 (Continued)

m/e	Relative Intensity
65	4
63	6



LXXV, X = SO

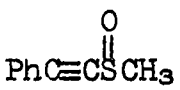
LXXVI, X = SO_2



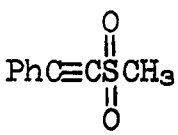
LXXVII

electron energies in all of the phenyl styryl sulfoxides and sulfones. Only one mode of fragmentation of this ion is found; loss of CO to form the m/e 91 ion. The 119 → 118 process either does not occur or is very diminuitive in these compounds.

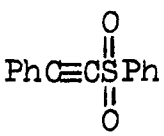
Since sp^2 hybridized carbons migrate from sulfur to oxygen whether they are part of an aromatic ring or a vinyl group, it seemed desirable to investigate the migratory ability of an sp carbon of an acetylenic group. Accordingly, LXXVIII, LXXIX and LXXX were investigated.



LXXVIII

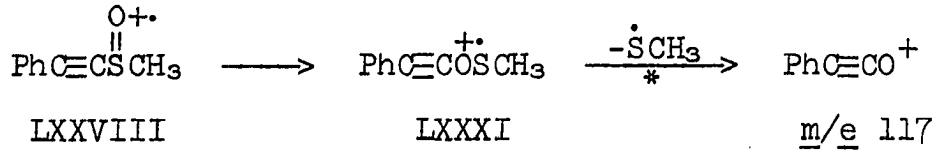


LXXIX



LXXX

An ion at m/e 117 is formed in the spectrum (Table 26) of LXXVIII by a one step loss of CH_3S. The sulfenate ion, LXXXI, is the likely precursor for the m/e 117 ion. The phenethynyl group apparently can migrate from sulfur to oxygen in the same manner as the styryl group. The m/e 117



LXXVIII LXXXI m/e 117

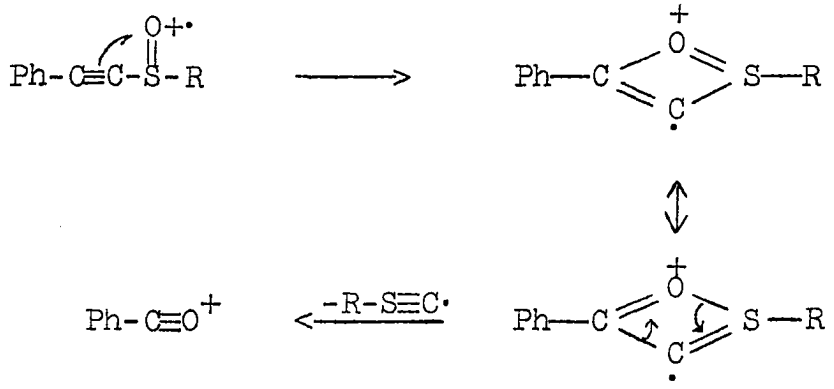
ion is also present in the spectrum of the two sulfones, LXXIX and LXXX.

The mode of fragmentation of the m/e 117 ion is interesting. A metastable ion indicates that carbon monoxide is lost to yield an ion at m/e 89, $C_7H_5^+$. This ion has appeared in other spectra (vide supra) and its structure is uncertain. A $(\text{tropylium-}H_2)^+$ analogue of the $(\text{cyclopentadienyl-}H_2)^+$ ion has been suggested for this ion (116) but its structure must be considered as unproven. Whatever its structure, it must be quite stable since it is the base peak in the spectrum of LXXIX.

Other fragmentations of LXXVIII are depicted in Figure 13. The ions at m/e 116, 115, and 103 are of unknown composition and structure. The m/e 105 ion is probably the benzoyl ion, $PhC{\equiv}O^+$. A rather esoteric mechanism may be written for its formation from the molecular ion.

Table 26. Mass spectra of LXXVIII and LXXIX

m/e	Relative Intensity LXXVIII	LXXIX
180		74
165		12
164	50	
149	100	3
148	6	
133	9	
121	29	3
117	17	14
116	11	
115	15	
105	10	8
103	11	4
102		6
89	46	100
77	46	11
75	11	15
74	12	10
69	10	
63	23	18
62	10	
51	23	11



This ion is present in the spectra of all three acetylenic compounds. A metastable ion for the $M^+ \rightarrow 105$ process in the spectrum of LXX (Table 27) indicates that it is occurring in one step in this compound. A metastable ion for the 105 → 77 process seems to confirm that the m/e 105 ion is the benzoyl cation.

An m/e 57 ion in the spectra of the methyl propenyl sulfoxide, LXXXI, and sulfone, LXXXII, and the allyl methyl sulfoxide, LXXXIII, and sulfone, LXXXIV, would indicate that migration from sulfur to oxygen of the unsaturated group is occurring. The methyl propenyl sulfoxide and sulfone were investigated to ascertain whether the phenyl group was somehow responsible for migration in the methyl styryl sulfoxides and sulfones. Occolowitz's recent discovery of vinyl group migration in methyl vinyl sulfoxide (66) made this work largely unnecessary.

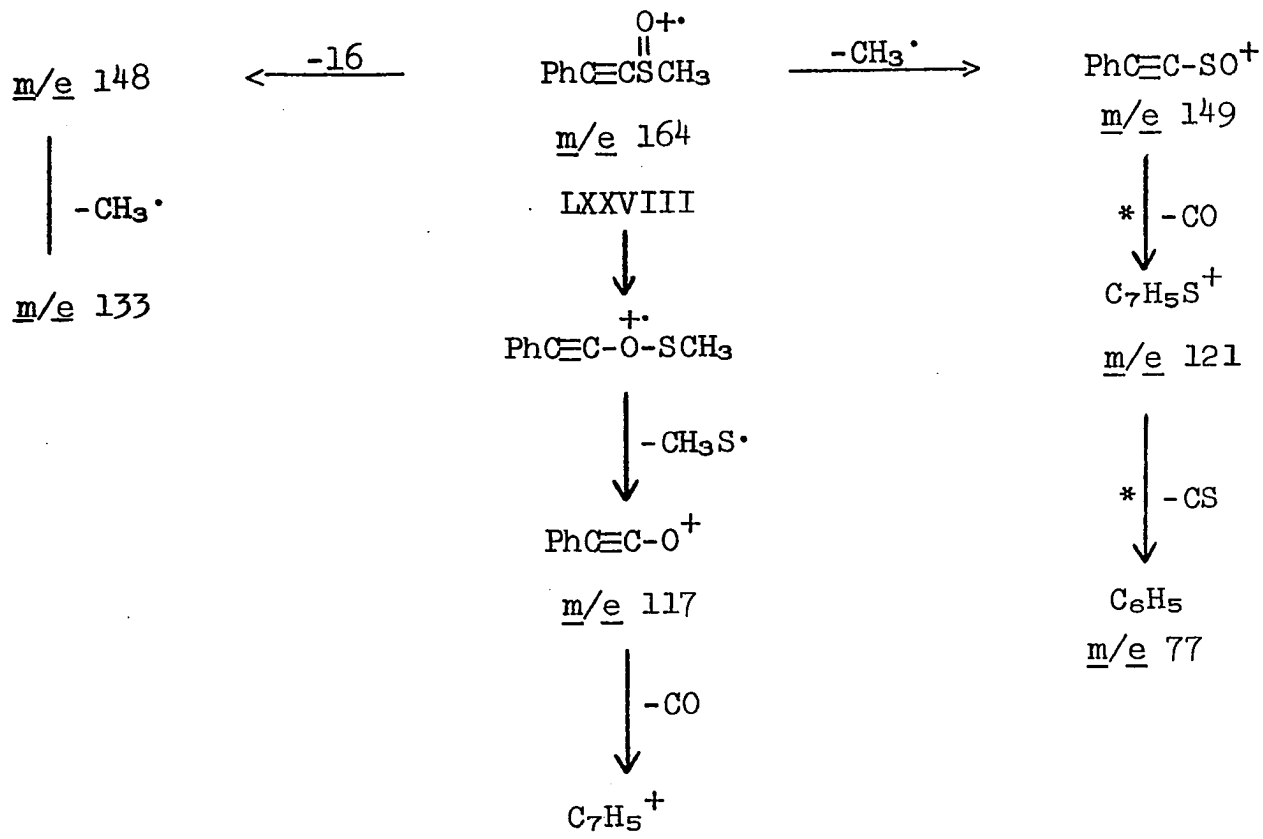


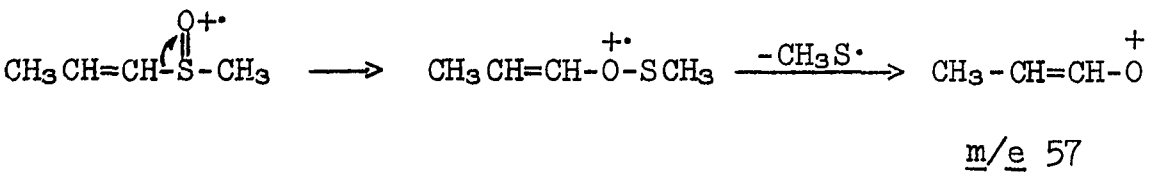
Figure 13. Fragmentation scheme of LXXVIII

Table 27. Mass spectrum of LXXX

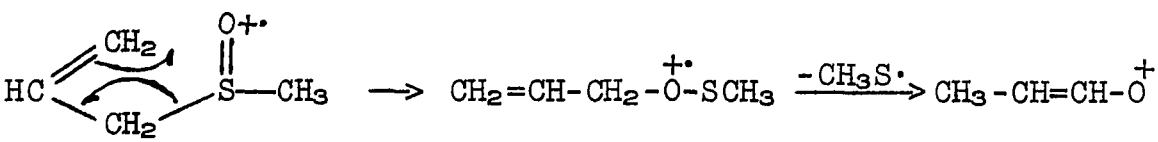
m/e	Relative Intensity
242 (M^+)	100
178	97
165	8
149	15
125	57
121	11
117	2
105	18
102	10
97	17
89	52
77	53
65	7
63	15
58	55
51	38

Mislow (60) has shown that sulfenates are formed thermally from allyl sulfoxides and the allyl sulfoxide and sulfone were investigated to determine if C-O bond formation occurred in electron impact induced ions.

Definitive work was not possible with the compounds studied since high resolution spectra were not available. An ion at m/e 57, however, indicates possible allyl and crotyl migration from sulfur to oxygen. Unfortunately, no



m/e 57



m/e 57

metastable ions, other than for 41 → 39, are present in the spectra to specify fragmentation pathways. Further work, expecially on allyl sulfoxides, is clearly indicated. The spectra of these compounds are given in Tables 28 and 29.

Table 28. Mass spectra of LXXXI and LXXXIII

m/e	Relative Intensity	
	LXXXI	LXXXIII
104	83	21
89	15	
87	27	
75	90	
73	24	
64	73	10
63		5
61	37	
57	12	
48	22	
47	27	
45	88	
43	78	
41	66	100
39	100	37

Table 29. Mass spectra of LXXXII and LXXXIV

	Relative Intensity	
m/e	LXXXII	LXXXIV
120	45	10
105	15	2
91	25	
80		1
79		1
65	10	1
64	32	2
63	15	2
58	22	
57	25	3
56		2
41	100	100
39	73	26

EXPERIMENTAL

General Procedures

All melting points and boiling points are uncorrected. Temperatures are given in degrees Centigrade. Mass spectra were recorded on an Atlas CH-4 single-focusing instrument. All samples were inserted directly into the source by means of a vacuum lock with liquids being adsorbed on silica gel for this purpose. The source was run at room temperature with as little heat as possible applied to the samples. The filament current was ca. five μamps and the accelerating voltage was three thousand volts.

The nmr and ir spectra were recorded on Varian A-60 and Perkin-Elmer 21 instruments, respectively. The nmr spectra were determined in deuteriochloroform solution and ir spectra were taken as potassium bromide discs. Nmr data are reported as follows: chemical shift (δ), signal multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), number of protons. Infrared absorptions are reported in microns.

Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

Ethers and Related Compounds

The following compounds were obtained from Drs. G. L. Eian and C. A. Kingsbury:

4-Bromophenyl 4-nitrophenyl ether

4-Chlorophenyl 4-nitrophenyl ether

4-(4-Nitrophenoxy)benzaldehyde

4-Phenoxynitrobenzene

4-(4-Nitrophenoxy)anisole

4-(4-Nitrophenoxy)toluene

4-Nitrophenyl 4-nitrophenyl ether

4-Thiophenoxynitrobenzene

4-Bromophenyl 4-nitrophenyl sulfide

4-Chlorophenyl 4-nitrophenyl sulfide

4-(4-Nitrothiophenoxy)aniline

The experimental procedure for preparing these compounds is available (117).

3-(4-Nitrophenoxy)toluene

Powdered potassium hydroxide (2.89 g, 0.04 mole) was added to a solution of m-cresol (4.32 g, 0.04 mole) in DMSO (20 ml). 4-Fluoronitrobenzene (4 ml) was added in one portion and the mixture was heated 30 minutes on a steam bath. Pouring into cold 2% sodium hydroxide solution was followed by several extractions with ether. The extracts

were washed with water, dried (magnesium sulfate), and concentrated on a rotary evaporator. Recrystallization (hexane) gave pure product, mp 62-63°, lit. mp 63° (118).

Recrystallization solvents, melting points, and C,H analyses (if necessary) are given for the remainder of the ethers prepared using this procedure.

4-Fluorophenyl 4-nitrophenyl ether

Benzene-hexane, mp 72-73.5°.

Anal. Calcd. for $C_{12}H_8FNO_3$: C, 61.80; H, 3.46. Found: C, 61.77; H, 3.52.

4-t-Butylphenyl 4-nitrophenyl ether

Benzene-hexane, mp 60.5-61.5°.

Anal. Calcd. for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32. Found: C, 70.83; H, 6.19.

4-Nitrophenyl 4-phenylphenyl ether

Benzene, mp 113-114°, lit. mp 120° (118).

Anal. Calcd. for $C_{18}H_{13}NO_3$: C, 74.21; H, 4.50. Found: C, 74.37; H, 4.59.

3-(4-Nitrophenoxy)aniline

Benzene, mp 78-79°, lit. mp 80-81° (119).

4-(4-Nitrophenoxy)benzonitrile

Ethyl acetate, mp 159.5-161°.

Anal. Calcd. for $C_{13}H_8N_2O_3$: C, 65.00; H, 3.36. Found: C, 64.84; H, 3.40.

3-(4-Nitrophenoxy)benzonitrile

Ethanol, mp 104.5-106°.

Anal. Calcd. for $C_{13}H_8N_2O_3$: C, 65.00; H, 3.36. Found: C, 64.99; H, 3.17.

4-(4-Nitrophenoxy)aniline

Ethanol-water, mp 132-133°, lit. mp 130-132° (120).

3-(4-Nitrophenoxy)anisole

Ethanol, mp 85-86°, lit. mp 86.5-87° (119).

3-Bromophenyl 4-nitrophenyl ether

Ethyl acetate-hexane, mp 52-53°.

Anal. Calcd. for $C_{12}H_8BrNO_3$: C, 49.00; H, 2.74. Found: C, 48.80; H, 2.73.

3-t-Butylphenyl 4-nitrophenyl ether

Hexane, mp 39-40°.

Anal. Calcd. for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32. Found: C, 70.59; H, 6.49.

3-Chlorophenyl 4-nitrophenyl ether

Hexane, mp 58-59°, lit. mp 61° (121).

3-(4-Nitrophenoxy)benzotrifluoride

Ethanol, mp 59-60°.

Anal. Calcd. for $C_{13}H_8F_3NO_3$: C, 55.13; H, 2.85. Found: C, 55.02; H, 2.86.

3-Fluorophenyl 4-nitrophenyl ether

Hexane, mp 70-71°.

Anal. Calcd. for $C_{12}H_8FNO_3$: C, 61.80; H, 3.46. Found: C, 62.12; H, 3.30.

4-Nitrophenyl 3-phenylphenyl ether

Ethanol, mp 64-65°.

Anal. Calcd. for $C_{18}H_{13}NO_3$: C, 74.21; H, 4.50. Found: C, 74.39; H, 4.63.

3-(4-Nitrophenoxy)phenyl phenyl ether

Ethanol, mp 63-64°.

Anal. Calcd. for $C_{18}H_{13}NO_4$: C, 70.35; H, 4.26. Found: C, 70.18; H, 4.18.

3-(4-Nitrophenoxy)phenol

3-(4-Nitrophenoxy)aniline was treated with nitrous acid and the resulting diazonium salt was hydrolyzed by the method of Vogel (122, p. 614). The product was recrystallized from ethanol, mp 95-96°, lit. mp 96-97° (123).

4-(4-Nitrophenoxy)phenol

4-(4-Nitrophenoxy)anisole was dissolved in benzene and a three-fold excess of anhydrous aluminum chloride was added. The mixture was stirred at reflux for 12 hours and poured on ice. The layers were separated; the water layer was extracted with ether which was combined with the benzene. This solution was thoroughly extracted with 10% sodium hydroxide solution. Acidification of this extract was followed by extraction with ether. The ether extract was dried (magnesium sulfate) and concentrated. The product was twice recrystallized from chloroform-hexane, mp 170-171°, lit. mp 173° (119).

4-(4-Nitrophenoxy)benzotrifluoride

4-Hydroxybenzotrifluoride was prepared by diazotizing 4-aminobenzotrifluoride and hydrolyzing the diazonium salt by boiling it in dilute sulfuric acid (122). The acid was continuously extracted with ether for three days. Evaporation of the ether extracts gave a quantitative yield of the crude phenol which was used directly in the preparation of the ether as previously described. The recrystallization solvent for the product was ethanol, mp 52-53°.

Anal. Calcd. for $C_{13}H_8F_3NO_3$: C, 55.13; H, 2.85. Found: C, 55.38; H, 2.75.

4-(4-Nitrophenoxy)butyrophenone (XXXIIIa)

4-Hydroxybutyrophenone was prepared by allowing n-butyric acid to react with an equimolar amount of phenol in polyphosphoric acid (PPA). The reactants were heated together on the steam bath for 15 minutes and poured on ice. After hydrolysis of the PPA was complete the mixture was extracted with ether. The extracts were washed with sat. sodium bicarbonate solution and water, dried over magnesium sulfate, and concentrated on a rotary evaporator to yield a yellow oil which solidified on cooling. It was slurried with hexane and filtered, giving a 40% yield of crude product, mp 86°, lit. mp 92° (124), which was reacted with 4-fluoronitrobenzene in the usual manner. The product was recrystallized from ethanol, mp 76-77°.

Anal. Calcd. for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30. Found: C, 67.54; H, 5.38.

4,4'-Oxydibutyrophenone (XXXV)

Diphenyl ether was treated with a two-fold excess of n-butyric acid in PPA as described by Brown and Capp (125). The compound was recrystallized from methanol, mp 101-102°, lit. mp 102-103° (125).

4,4'-Oxydivalerophenone (XXXVII)

n-Valeric acid was reacted with phenol in PPA in the same manner as for 4,4'-oxydibutyrophenone. The recrystal-

lization solvent was ethanol, mp 97.5-99°, lit. mp 98-99° (125).

4,4'-Dibutyrophenone (XXXVI)

Biphenyl was reacted with n-butyryl chloride in the presence of anhydrous aluminum chloride with carbon disulfide as the solvent in the method described by Long and Henze (126). Three recrystallizations from chloroform-hexane gave the product with a mp of 172-173°, lit. mp 174.2 (126).

4,4'-Divalerophenone (XXXVIII)

The procedure for preparing 4,4'-dibutyrophenone was followed for this compound using n-valeric rather than n-butyric acid. Recrystallization was from benzene, mp 161-162°, lit. mp 163° (126).

4-(4-Nitrophenoxy)valerophenone (XXXIIIb)

4-Hydroxyvalerophenone was prepared by the same procedure used for 4-hydroxybutyrophenone and reacted with 4-fluoronitrobenzene as usual. Ethanol was used to recrystallize the product, mp 54-55°.

Anal. Calcd. for $C_{17}H_{17}NO_4$: C, 68.21; H, 5.73. Found: C, 68.36; H, 5.69.

1,4-Di-(4-nitrophenoxy)benzene (XXIX)

Hydroquinone (8.8 g) was dissolved in 100 ml of DMSO and treated with 14 g of powdered potassium hydroxide and

18 ml of 4-fluoronitrobenzene. This mixture was heated on the steam bath for 45 minutes and poured on ice. The solid which formed was collected by filtration and washed with 10% sodium hydroxide solution, water, and ether (to remove 4-fluoronitrobenzene). Twenty-six grams of crude product was obtained. Recrystallization from dioxane gave pure product, mp 232-234°, lit. mp 232-234° (127).

1,3-Di-(4-nitrophenoxy)benzene (XXX)

Resorcinol was reacted with potassium hydroxide and 4-fluoronitrobenzene as described above. The product was recrystallized from benzene-hexane, mp 117-119°.

Anal. Calcd. for $C_{18}H_{12}N_2O_6$: C, 61.36; H, 3.44. Found: C, 61.32; H, 3.35.

4-(4-Nitrophenoxy)phenyl phenyl ether

4-Phenoxyphenol was prepared by hydrolyzing 4-phenoxyphenyl diazonium sulfate in the manner of Vogel (122, p. 614).

The crude phenol was reacted with 4-fluoronitrobenzene in the usual manner. The product ether was recrystallized from ethanol-water, mp 88-90°.

Anal. Calcd. for $C_{18}H_{13}NO_4$: C, 70.35; H, 4.26. Found: C, 70.21; H, 4.37.

4-n-Valerylphenyl 4-n-butyrylphenyl ether (XXXIX)

n-Valeryl chloride (12 g, 0.10 mole) was added dropwise to a stirred solution of phenyl ether (21 g, 0.13 mole) in 100 ml of carbon disulfide, with anhydrous aluminum chloride (13.2 g, 0.10 mole) present as catalyst. The mixture was stirred four hours, the solvent evaporated and the mixture poured on ice and extracted with ether. The extracts were washed with 10% sodium hydroxide solution and water, dried (magnesium sulfate), and concentrated to give a two-component oil (by tlc). The oil was chromatographed on silica gel with carbon tetrachloride elution. Three grams of pure (by nmr) 4-phenoxyvalerophenone was obtained after unreacted phenyl ether had been eluted.

The compound gave the following nmr spectrum: δ 1.0, t, 3H; 1.2-2.0, m, 4H; 2.8, t, 2H; 6.7-7.9, m, 9H.

The mono-substituted ether was mixed with an equimolar amount of n-butyric acid in PPA, heated (steam bath) for 30 minutes and poured on ice. The solid which formed was collected and washed with 10% sodium hydroxide solution and water. Ethanol was used as the recrystallization medium, mp 86-87°. The nmr spectrum had the following resonances: δ 1.0, perturbed t, 6H; 1.2-2.0, m, 6H; 2.9, t, 4H; 7.1, d, 4H; 8.0, d, 4H.

Anal. Calcd. for $C_{21}H_{24}O_3$: C, 77.75; H, 7.46. Found: C, 78.01; H, 7.58.

3,5-Dinitrophenyl 4-nitrophenyl ether (XXVIII)

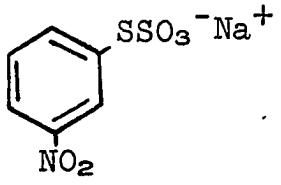
3,5-Dinitrophenol was prepared from 3,5-dinitroanisole by the method of Sidgwick and Taylor (128).

The crude phenol was reacted with 4-fluoronitrobenzene as previously described. The product was recrystallized from ethanol, mp 144.5-145.5°.

Anal. Calcd. for $C_{12}H_7N_3O_7$: C, 47.22; H, 2.31. Found: C, 47.14; H, 2.26.

3-(4-Nitrothiophenoxy)aniline

Sodium S-3-nitrophenyl thiosulfate was prepared by the



method of Lecher and Hardy (129). A mixture of 12.4 g of sodium bisulfite, 10 ml water, 9.2 g bis-(3-nitrophenyl)-disulfide, and 150 ml of methanol was stirred at reflux two hours. Sodium hydroxide (1.2 g) was added to convert excess sodium bisulfite to sodium sulfite. The mixture was filtered at room temperature and the residue was washed with 50 ml of methanol. The combined filtrates were evaporated and the residue was treated with 200 ml of dry methanol. Filtration and removal of the methanol yielded the product as a light-brown solid.

Six grams of this material was mixed with 75 ml of concentrated hydrochloric acid and stirred vigorously overnight. An oil separated during this operation. The mixture was poured on ice and extracted with benzene. The extracts were dried (magnesium sulfate) and concentrated, leaving a yellow oil. The mass spectrum of this compound indicated that it was m-nitrothiophenol, slightly contaminated with the corresponding disulfide.

m-Aminothiophenol was prepared by the method of Vogel (122, p. 563). Six grams of m-nitrothiophenol and eleven grams of granulated tin were mixed and 25 ml of concentrated hydrochloric acid added in portions with shaking and cooling. After completion of the reaction, the mixture was poured into water and neutralized with sodium hydroxide. Steam distillation was followed by saturation of the distillate with sodium chloride and two extractions each with benzene and ether. The combined extracts were dried (magnesium sulfate) and concentrated, leaving 370 mg of light-yellow oil. The mass spectrum contained a molecular ion at m/e 125.

This compound (370 mg) was dissolved in 10 ml of absolute ethanol and treated with 70 mg of sodium in small portions. When all of the sodium had dissolved, 0.3 ml of 4-fluoronitrobenzene was added and the mixture was stirred at reflux for five hours. The mixture was poured on ice and

extracted with ether. The extracts were washed with water, dried over magnesium sulfate, and concentrated. The solid which remained (300 mg) was recrystallized from ethanol-water, mp 94-96°. Mass spectrum: M^+ at m/e 246.

Anal. Calcd. for $C_{12}H_{10}N_2O_2S$: C, 58.52; H, 4.09. Found: C, 58.60; H, 4.12.

4-(4-t-Butylphenoxy)butyrophenone (XL)

Diphenyl ether was alkylated with t-butyl chloride in carbon disulfide in the presence of aluminum chloride. The p-phenoxy-t-butylbenzene was contaminated with a small amount of diphenyl ether which could not be separated.

The product was treated with valeryl chloride and aluminum chloride in carbon disulfide. The crude product was chromatographed on silica gel. Elution with hexane yielded p-phenoxy-t-butylbenzene. A 95% hexane-5% ethyl acetate mixture eluted the product which was slightly contaminated with 4,4'-oxydibutyrophenone.

Organosulfur Compounds

The following compounds were obtained from Dr. Leo Ochrymowycz and the procedures for their preparation are available (94):

α-(Methylsulfinyl)propiophenone (LVII)

α-(Methylsulfonyl)propiophenone (LVIII)

ω-(Methylsulfenyl)acetophenone (LI)

Methyl-(α-phenylstyryl)sulfoxide (LXVIII)

Methyl-(α-phenylstyryl)sulfone (LXXI)

Methyl-(α-methylstyryl)sulfoxide (LXVI)

Methyl-(α-ethylstyryl)sulfoxide (LXVII)

Methyl-(β-methylstyryl)sulfoxide (LXV)

Methyl-(β-methylstyryl)sulfone (LXX)

Methyl phenethynyl sulfoxide (LXXVIII)

Methyl phenethynyl sulfone (LXXIX)

ω-(Methylsulfinyl)acetophenone (XLIa)

The procedure of Corey and Chaykovsky (130) was followed. A one-liter three-necked flask was equipped with stirrer, condenser, and pressure equalizing addition funnel. The apparatus was flame dried and all operations were conducted under nitrogen. A mineral oil dispersion of sodium hydride (47 g, 53% NaH, ca. 1.0 mole) was added to the flask and washed three times with pentane. One pint of freshly opened DMSO was added slowly and the mixture was heated two hours at 65° to form the dimsyl anion. Ethyl benzoate (70 ml, ca. 0.5 mole) was added dropwise to the cooled solution. The mixture was stirred six hours at room temperature and poured on ice. Acidification with hydrochloric acid was followed

by extraction with chloroform. The extracts (ca. 1300 ml) were washed with water, dried over magnesium sulfate, and concentrated. The oil which remained was taken up in chloroform and treated with hexane to effect crystallization. The product (50 g) was collected by filtration, mp 83.5-84.5°, lit. mp 86-86.5° (130).

ω,ω-Dideuterio-ω-(methylsulfinyl)acetophenone (XLIb)

One gram of ω-(methylsulfinyl)acetophenone was dissolved in 50 ml of deuterium oxide. A trace of potassium carbonate was added, the mixture was stirred for one hour, then thoroughly extracted with chloroform. The extracts were dried over magnesium sulfate and concentrated. The product was slurried with cold ether and filtered, mp 80-83°. Low voltage mass spectra showed the deuterium content to be as follows: d_0, 3.5%; d_1, 18.9%; d_2, 77.6%.

ω-(Methyl-d_3-sulfinyl)acetophenone (XLIc)

DMSO-d_6 (10 ml) was reacted with sodium hydride (0.5 g). The dimsyl-d_6 sodium was treated with ethyl benzoate and worked up as usual. The product was exchanged in water containing a trace of potassium carbonate to give ω-(methyl-d_3-sulfinyl)acetophenone, mp 83-85°. Deuterium content: d_2, 3.7%; d_3, 96.3%.

ω-(Methylsulfonyl)acetophenone (XLVI)

ω-(Methylsulfinyl)acetophenone (1.8 g) was dissolved in 10 ml of glacial acetic acid. Five ml of 30% hydrogen peroxide was added and the mixture was heated 30 minutes on the steam bath. After standing 12 hours at room temperature, the mixture was poured into water and extracted with chloroform. The extracts were dried (magnesium sulfate) and concentrated. The solid which remained was recrystallized twice from ethyl acetate-hexane, mp 100-101°, lit. mp 106-107° (131). Another recrystallization from ethanol-chloroform did not raise the melting point. The reason for the low melting point is not known, since the compound was pure by tlc and spectral criteria. Ir: 5.97 μ (C=O); 7.70 and 8.68 μ ($-SO_2-$). Nmr: δ 3.1, s, 3H; 4.6, s, 2H; 7.4-8.1, m, 5H.

ω-Methoxyacetophenone (L)

This compound was purchased from Aldrich Chemical Co. and purified by preparative vpc (SE-30 column, 175°).

ω-(Benzylsulfenyl)acetophenone (LIII)

The sodium salt of benzyl mercaptan was prepared by adding 36 g of the mercaptan to a solution of 10 g of sodium hydroxide in 40 ml of water. The solution was cooled and stirred vigorously while 39 g of ω-chloroacetophenone was added. The mixture solidified and was extracted with ether.

The ether was washed with 10% hydrochloric acid and water, dried (magnesium sulfate), and concentrated. A yellow solid remained (38 g). Recrystallization from ethanol gave the product, mp 85-87°. Nmr: δ 3.6, s, 2H; 3.7, s, 2H; 7.2-8.0, m, 10H.

LIII was reduced to the β-hydroxy sulfide, LXXXV, by sodium borohydride. Fifteen grams of LIII was dissolved in 150 ml of hot methanol. Sodium borohydride (1.0 g) was added in portions to the hot solution. A vigorous reaction ensued. Since part of the reducing agent probably reacted with the hot methanol, the mixture was allowed to stand overnight and another gram of sodium borohydride was added. The mixture was stirred for six hours and concentrated. Two hundred ml of water was added and the mixture was extracted with ether. The extracts were dried over magnesium sulfate and concentrated. The solid which remained was recrystallized from benzene-hexane, 13 g, mp 45-48°. Nmr: δ 3.6-3.8, m, 2H; 2.98, s, 1H (OH); 3.7, s, 2H; 4.7, q, 1H; 7.3, s, 10H. Mass spectrum: M^+ at m/e 274.

ω-(Benzylsulfinyl)acetophenone (LIV)

The β-hydroxysulfide was converted to β-hydroxysulfoxide, LXXXVI, with m-chloroperbenzoic acid. LXXXV (2.6 g, 10 mmole) was dissolved in 50 ml of chloroform and 1.72 g (10 mmole) of m-chloroperbenzoic acid was added in portions to the

cooled, stirred solution. The mixture was allowed to stand overnight (refrigerator), then washed with sat. sodium bicarbonate solution and water, dried over magnesium sulfate, and concentrated. The white solid which remained was recrystallized from ethyl acetate-hexane, mp 113-135° (diastereomers). Ir: 3.08 μ (-OH); 9.54 μ (-SO-).

One hundred milligrams of LXXXVII was dissolved in 10 ml of acetone and activated manganese dioxide (1.0 g) (132) was added. The mixture was allowed to stand for six hours with occasional shaking and then was gravity filtered. The precipitate was washed with 50 ml of acetone and the combined filtrates were evaporated. The product was recrystallized from chloroform-hexane, mp 130-132°. Ir: 5.98 μ (C=O); 9.64 μ (-SO-).

ω-(Benzylsulfonyl)acetophenone (LII)

One gram of LXXXVII was dissolved in 25 ml of glacial acetic acid and five ml of 30% hydrogen peroxide was added slowly. The mixture was allowed to stand overnight, then poured over ice and filtered. The white crystals were recrystallized from acetone-water, mp 179.5-180.5. The ir spectrum of the β-hydroxysulfone had the following absorptions: 2.89 μ (-OH); 7.73 and 8.92 μ ($-SO_2-$).

The β-ketosulfone, LII, was prepared by manganese dioxide oxidation of the β-hydroxysulfone. Recrystallization from chloroform-hexane gave LII, mp 108-110°.

Anal. Calcd. for $C_{15}H_{14}O_3S$: C, 65.67; H, 5.14. Found: C, 65.42; H, 5.03.

α-(Methylsulfinyl)butyrophenone (LV)

To 1.08 g of sodium methoxide in 50 ml of dry THF was added 3.6 g of ω-(methylsulfinyl)acetophenone in 20 ml of THF. The mixture was heated at reflux for 30 minutes. Two ml of ethyl iodide was added and the reaction was maintained at reflux overnight. The mixture was poured over ice and extracted with chloroform. The extracts were dried (magnesium sulfate) and concentrated. The oil which remained was chromatographed on silica gel and developed with ethyl acetate. Two unidentified by-products were eluted before the product was obtained as a colorless oil. Nmr: δ 1.08, t, 3H; 2.1, m, 2H; 2.5, s, 3H; 4.6-4.9, m, 1H; 7.4-82., m, 5H.

α-(Methylsulfonyl)butyrophenone (LVI)

α-(Methylsulfinyl)butyrophenone was oxidized with hydrogen peroxide in the usual manner. The product was recrystallized from ethyl acetate-hexane, mp 111-112°. Nmr: δ 1.0, t, 3H; 2.3, quintet, 2H; 2.9, s, 3H; 4.8 t, 1H; 7.4-8.2, m. 5H. Ir: 5.96 μ (C=O); 7.76 and 8.73 μ ($-SO_2-$).

Anal. Calcd. for $C_{11}H_{14}O_3S$: C, 58.38; H, 6.24. Found: C, 58.22; H, 6.23.

Methyl styryl sulfoxide (LIX)

ω-(Methylsulfinyl)acetophenone (15 g) was dissolved in 50 ml of water and cooled with an ice-bath. One gram of sodium borohydride was added in portions, the mixture was stirred two hours at room temperature and then thoroughly extracted with chloroform. The extracts were dried over magnesium sulfate and concentrated. The oil which remained was crystallized from benzene-hexane (13.5 g), then recrystallized from ethyl acetate, mp 78-105° (diastereomers), lit. mp 78-123° (91).

This β-hydroxysulfoxide (9.2 g, 0.05 mole) was dissolved in 100 ml of dry THF. This solution was added to a slurry of sodium hydride-mineral oil (2.0 g, 53% NaH) in 25 ml of THF. The mixture was stirred 30 minutes at room temperature and 7.1 g (0.05 mole) of methyl iodide was added. Stirring was continued for 30 minutes, methanol was added to quench excess sodium hydride, and the mixture was concentrated. The oil that remained was taken up in ether, washed with water, dried (magnesium sulfate) and reconcentrated. The β-methoxy sulfoxide was a light brown oil.

Elimination of methanol from the β-methoxy sulfoxide was accomplished by heating with sodium hydride. To a suspension of one gram of sodium hydride in 25 ml of dry THF was added a solution of the β-methoxy sulfoxide (3.4 g) in 50 ml of THF. The mixture was heated at reflux one hour,

poured into water, and extracted with chloroform. The extracts were dried over magnesium sulfate and concentrated, leaving a light brown oil. The oil was taken up in ethyl acetate and enough hexane added to induce clouding. Chilling caused the product to separate as white crystals which were recrystallized from ether, mp 61.5-63°, lit. mp 61-62° (91).

Methyl-d_3-(β-deuteriostyryl)sulfoxide (LXIII)

One gram of methyl styryl sulfoxide was dissolved in 10 ml of dioxane and mixed with 10 ml of deuterium oxide in which 0.5 g of sodium had been dissolved. This mixture was heated at reflux 12 hours and concentrated. The residue was taken up in chloroform. The chloroform solution was dried (magnesium sulfate) and concentrated. The solid which remained was recrystallized from ether, mp 62-63°. Deuterium content: d_2, 1.1%; d_3, 10.9%; d_4, 88.0%.

Methyl-(α-deuteriostyryl)sulfoxide (LXII)

This compound was prepared in three steps from ω-(methylsulfinyl)acetophenone as previously described. Sodium borodeuteride was used in the initial step to effect the labelling. The melting point of the product was 62-64°. Deuterium content: d_0, 4.7%; d_1, 95.3%.

Methyl-d_3-(α,β-dideuteriostyryl)sulfoxide (LXIV)

LXII was exchanged with sodium in deuterium oxide as previously described. The melting point was 63-64°. Deuterium content: d_1, 1.6%; d_4, 8.1%; d_5, 90.3%.

Methyl styryl sulfone

Methyl styryl sulfoxide (LIX) was oxidized with 30% hydrogen peroxide in the usual manner. The product was recrystallized from ethanol, mp 76-78°, lit. mp 77-79° (91).

Methyl phenylthiolacetate (LXI)

Phenylacetic acid was treated with excess thionyl chloride and the mixture was heated 30 minutes (steam bath). Unreacted thionyl chloride was removed on the rotary evaporator and the crude acid chloride was dissolved in dichloromethane. A dry ice-acetone condenser was attached to the flask and methyl mercaptan (excess) was added while nitrogen was swept through the system. The mixture was stirred two hours, methyl mercaptan and dichloromethane were removed at aspirator vacuum, and the residue was taken up in ether. The ether solution was washed with sat. sodium bicarbonate solution and water, dried (magnesium sulfate), and concentrated. The pure product was obtained by distillation at 120-121° (14 mm), lit. bp 126° (11 mm) (133). Nmr: δ 2.1, s, 3H; 3.7, s, 2H; 7.2, s, 5H.

Phenyl styryl sulfoxide (LXXII)

Phenyl styryl sulfide was prepared in 90% yield by the reaction of phenylacetylene with thiophenol in the method of Oswald, *et al.* (134). The material was *ca.* 50:50 *cis*:*trans* according to the nmr spectrum (134). Attempts to prepare a solid sulfoxide from this mixture failed, so preparation of a pure isomer was attempted.

The mixture of *cis*:*trans* isomers described above was heated overnight at *ca.* 80° in heptane with a trace of thiophenol. Removal of the heptane showed that the *trans*:*cis* ratio had increased to 2.5:1 (nmr). This operation was repeated twice more to give a phenyl styryl sulfide mixture which was 85% *trans*. This was chromatographed on silica gel and eluted with hexane.

This material was oxidized with an equimolar amount of m-chloroperbenzoic acid in the usual manner. The crude product was chromatographed on silica gel. Elution with hexane gave a small amount of unreacted sulfide and ethyl acetate eluted the sulfoxide. The sulfoxide was *ca.* 89% *trans* isomer (nmr). One vinyl proton was hidden by the aromatic proton absorptions, but the other proton appeared as a doublet (J = 15.5 Hz, *trans*) at δ 6.8 and another doublet (J = 11.0 Hz, *cis*) at δ 6.4.

Crystallization occurred when the oil was taken up in ethyl acetate, hexane added to cloudiness, and chilled.

The nmr spectrum indicated this material was 100% *trans* sulfoxide. Three recrystallizations from ethyl acetate-hexane resulted in material with a melting point of 60-61.5°. According to the mass spectrum the product was slightly (<3%) contaminated with M + 16 material (probably sulfone). Ir: 9.63 μ (-SO-).

Phenyl styryl sulfone (LXXIII)

Phenyl styryl sulfide (*ca.* 50:50 *cis*:*trans*) was oxidized with 30% hydrogen peroxide in the usual manner. The product was an oil which crystallized after two weeks in the refrigerator. The product was recrystallized from ethyl acetate-hexane, mp 72.5-74°, lit. mp 74-75° (*trans*) (135).

4-Bromophenyl styryl sulfoxide (LXXV)

Phenyl acetylene and p-bromothiophenol were reacted as described in the literature (134). The sulfide was recrystallized from heptane, mp 73-75°, lit. mp 74-76° (*cis*) (134). The nmr spectrum was identical to the published spectrum of the *trans* isomer (134).

Oxidation with m-chloroperbenzoic acid in the usual manner gave a solid which was recrystallized from benzene-hexane, mp 100-101°. Ir: 9.62 μ (-SO-).

4-Bromophenyl styryl sulfone (LXXVI)

4-Bromophenyl styryl sulfoxide was oxidized with hydrogen peroxide as usual. The product was recrystallized from ethanol-water, mp 99-100°. Ir: 7.62 and 8.78 μ ($-SO_2-$).

Anal. Calcd. for $C_{14}H_{11}BrO_2S$: C, 52.02; H, 3.43. Found: C, 52.03; H, 3.31.

4-Nitrophenyl styryl sulfone (LXXVII)

The sulfide was prepared as follows: p-nitrothiophenol (7.75 g) was mixed with five ml of phenylacetylene and a trace of 2,2′-azo-bis-isobutyronitrile in 80 ml of benzene. This mixture was heated at reflux for 24 hours. Thorough extraction with 10% sodium hydroxide solution was followed by washing with water, drying (magnesium sulfate), and concentration. The brown solid (4.0 g) was slurried with ethanol and filtered, mp 93-100°. Recrystallization (acetone-water) did not change the melting point. The mass spectrum contained an ion at m/e 308 (probably M^+ of the disulfide). Ir: 6.64 and 7.51 μ ($-NO_2$).

Oxidation with hydrogen peroxide in the usual manner gave 4-nitrophenyl styryl sulfone. Ethanol was the recrystallization medium, mp 119-121°. No ions higher than m/e 300 were observed in the mass spectrum. Ir: 6.55 μ ($-NO_2$); 8.78 μ ($-SO_2-$); 7.42 μ ($-NO_2$ or $-SO_2-$); 7.73 μ ($-SO_2-$ or $-NO_2$).

Anal. Calcd. for $C_{14}H_{11}NO_4S$: C, 58.12; H. 3.83. Found: C, 58.09; H, 3.78.

Phenyl phenethynyl sulfone (LXXX)

The sulfide was prepared by bromination and double dehydrobromination of phenyl styryl sulfide.

Phenyl styryl sulfide was dissolved in carbon tetrachloride and treated with an equimolar amount of bromine in carbon tetrachloride. After six hours of stirring at room temperature, sodium bisulfite solution was added until the bromine color disappeared. The solution was washed with water, dried (magnesium sulfate), and concentrated, leaving a green oil. This oil was heated at reflux for one hour with an excess of potassium hydroxide in 95% ethanol. Concentrated hydrochloric acid was added to neutralize the base and the mixture was filtered. The filtrate was concentrated, water was added to the residue followed by extraction with ether. The extract was washed with water, dried (magnesium sulfate), and concentrated. Distillation gave a ca. 10% yield of phenyl phenethynyl sulfide, bp 127° (0.3 mm), Ir: 4.63 μ (-C≡C-); lit. bp 155-170° (2.5 mm), Ir: 4.65 μ (136).

The sulfide (0.42 g, 2 mmole) was dissolved in 10 ml of chloroform, cooled, and treated with 0.69 g (4 mmole) of m-chloroperbenzoic acid in 20 ml of chloroform. After seven

days of refrigeration the mixture was extracted with sat. sodium bicarbonate solution and water, dried (magnesium sulfate) and concentrated. A light-yellow oil which crystallized on cooling was the product. The sulfone was recrystallized from ethyl acetate-hexane, mp 71-73°, Ir: 4.59 μ (-C≡C-); 7.57 and 8.66 μ ($-SO_2-$); lit. mp 73-74°, Ir: 4.65 μ (136).

Methyl propenyl sulfoxide (LXXXI)

Methyl propenyl sulfide was prepared from allyl methyl sulfide by the procedure of O'Connor and Lyness (137).

The sulfoxide was prepared by oxidation of methyl propenyl sulfide in the usual manner with m-chloroperbenzoic acid. The nmr spectrum was identical to the literature spectrum (137).

Methyl propenyl sulfone (LXXXII)

Methyl propenyl sulfide was oxidized with hydrogen peroxide to give the desired product with the same nmr spectrum as reported previously (137).

Allyl methyl sulfoxide (LXXXIII)

Allyl methyl sulfide was oxidized with m-chloroperbenzoic acid as usual. The compound had the same nmr spectrum as previously prepared material (137).

Allyl methyl sulfone (LXXXIV)

Allyl methyl sulfide was oxidized with hydrogen peroxide to give a product whose nmr spectrum was identical to the literature spectrum (137).

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APPENDIX

Suggestions for Further Research

Charge localization and transfer

In view of the apparent transmission of electronic effects through sulfur in thioethers, it is desirable that other thioethers with electron-donating groups such as hydroxy and methoxy on ring B be prepared. The question of charge localization vs. resonance stabilization of the product ion might be clarified with these compounds.

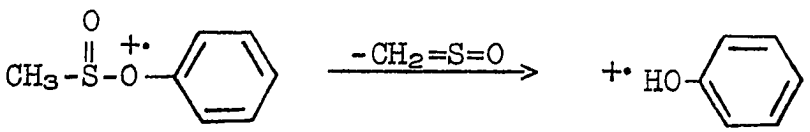
It would be interesting to know the IP of the molecules and the AP of NO· loss in the ethers studied, but a source with a more monoenergetic electron beam is needed. The IP's of these compounds will be difficult to determine in any case since they are all solids.

Rearrangements in β-ketosulfoxides and β-ketosulfones

One more attempt to observe competitive olefin and sulfine loss from the same molecule might be made with methylsulfinylmethyl n-propyl ketone. A similar compound has been prepared (131) and the synthesis by the reaction of dimsyl anion with ethyl butyrate should be straight forward.

$$CH_3(CH_2)_2COCH_2SOCH_3$$

Since the loss of sulfene from methyl sulfonates has been suggested, it would be of interest to observe the spectrum of phenyl methyl sulfinate to see if sulfine loss occurs readily, as would be expected.



The McLafferty rearrangement corresponds to the photochemical Norrish Type II rearrangement and it would be interesting to determine whether the rearrangement would occur in molecules where the expelled fragment is a sulfine or sulfene. The rearrangement has been observed upon photolysis of β-ketoethers (138), and β-ketothioethers (139). One attempt to observe sulfene formation by photolysis of a β-ketosulfone was not successful (140), but it seems that further effort would be worthwhile.

Further studies on the 120 $\xrightarrow{*}$ 91 process would be desirable, since the acetophenone enol ion loses CHO· in some instances, but not in others.

Rearrangements in unsaturated sulfoxides and sulfones

The question of C-O bond formation in allylic sulfoxides and sulfones should be investigated more thoroughly with

additional compounds. Allylic sulfoxides are racemized through sulfenate intermediates (60) and the preliminary results given in this thesis indicate that sulfenate ions may be a product of rearrangement in mass spectral ions.

The photolytic and pyrolytic behavior of organic molecules often resembles their behavior upon electron impact. The styryl sulfoxides, which appear to form benzofuran molecular ion in the mass spectrometer, might yield this species upon photolysis or thermolysis.

The nature of the m/e 89 ion should be investigated more thoroughly by thermochemical and labelling data to determine its structure.

Of limited interest is the origin of the carbon atom that is lost as CO from styryl sulfoxides. Labelling with ^{13}C will be necessary to make an unambiguous assignment.